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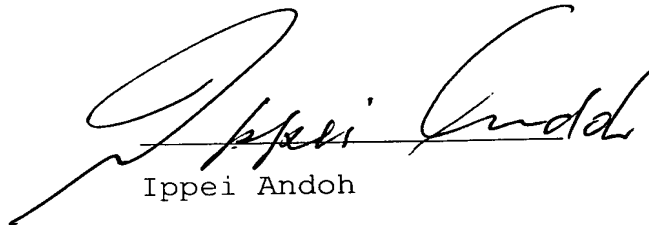
DECLARATION

I, Ippei Andoh, having an address of c/o CHEMPATENT, LTD., Tamura Bldg. 5<sup>th</sup> Floor, 4-23-17, Higashi-Ikebukuro, Toshima-ku, Tokyo, Japan, hereby declare that I have competent knowledge of the Japanese and English languages, and that I have made the accompanying translation of JAPANESE PATENT APPLICATION NO. 2000-108824 filed on April 6, 2001 in the name of JSR Corporation, and that the said translation is true and correct to the best of my knowledge and belief and that this declaration was made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

DECLARED by said Ippei Andoh

at Tamura Bldg. 5<sup>th</sup> Floor, 4-23-17, Higashi-Ikebukuro, Toshima-ku,  
Tokyo, Japan

This 13th day of June, 2003

  
Ippei Andoh

PATENT OFFICE  
JAPANESE GOVERNMENT

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This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Application Number:	108824/2001 ✓
Applicant(s):	JSR Corporation INTERNATIONAL BUSINESS MACHINES CORPORATION

June 6, 2001

Commissioner, Patent Office  
Kozo OIKAWA

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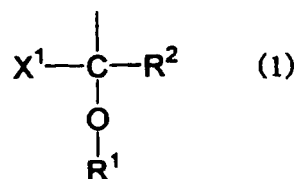
[Document Name] Specification

[Title of the Invention] RADIATION-SENSITIVE RESIN COMPOSITION

[Claims]

[Claim 1] A radiation-sensitive resin composition comprising (A) an acid-dissociating group-containing resin having a structure represented by the following formula (1) and (B) a photoacid generator:

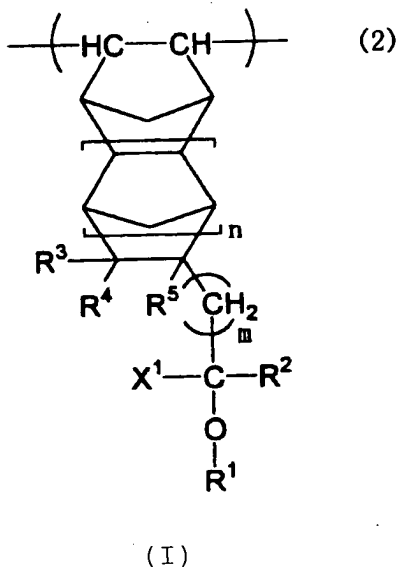
[Formula 1]



wherein  $\text{R}^1$  represents a hydrogen atom, a monovalent acid-dissociable group, an alkyl group having 1-6 carbon atoms which does not have an acid-dissociable group, or an alkylcarbonyl group having 2-7 carbon atoms which does not have an acid-dissociable group,  $\text{X}^1$  represents a linear or branched fluoroalkyl group having 1-4 carbon atoms, and  $\text{R}^2$  represents a hydrogen atom, a linear or branched alkyl group having 1-10 carbon atoms, or a linear or branched fluoroalkyl group having 1-10 carbon atoms.

[Claim 2] A radiation-sensitive resin composition comprising (A) an acid-dissociating group-containing resin having a recurring unit (I) represented by the following formula (2) and (B) a photoacid generator:

[Chemical Formula 2]

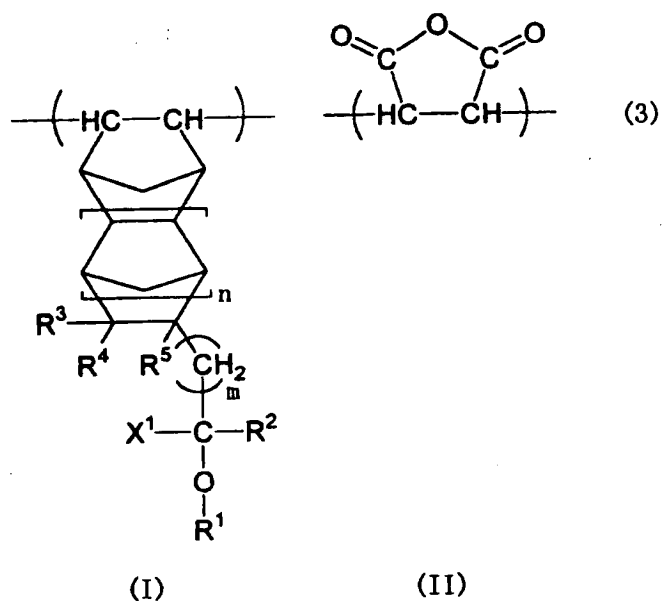


wherein  $R^1$  represents a hydrogen atom, a monovalent acid-dissociable group, an alkyl group having 1-6 carbon atoms which does not have an acid-dissociable group, or an alkylcarbonyl group having 2-7 carbon atoms which does not have an acid-dissociable group,  $X^1$  represents a linear or branched fluoroalkyl group having 1-4 carbon atoms,  $R^2$  represents a hydrogen atom, a linear or branched alkyl group having 1-10 carbon atoms, or a linear or branched fluoroalkyl group having 1-10 carbon atoms,  $R^3$ ,  $R^4$ , and  $R^5$  individually represent a hydrogen atom, a linear or branched alkyl group having 1-4 carbon atoms, a monovalent oxygen-containing polar group, or a monovalent nitrogen-containing polar group,  $n$  is an integer of 0-2, and  $m$  is an integer of 0-3.

[Claim 3] A radiation-sensitive resin composition

comprising (A) an alkali insoluble or scarcely soluble acid-dissociating group-containing resin having a recurring unit (I) and a recurring unit (II) shown by the following formula (3) and (B) a photoacid generator:

[Chemical Formula 3]

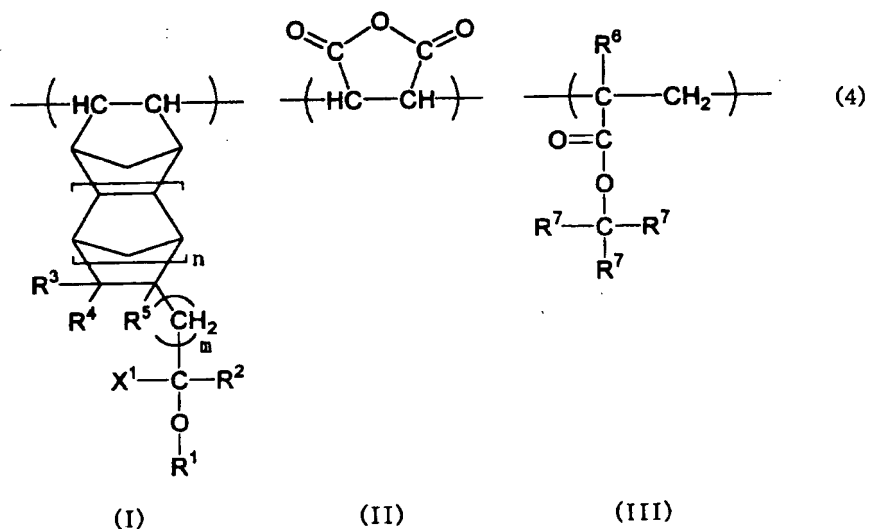


wherein  $R^1$  represents a hydrogen atom, a monovalent acid-dissociable group, an alkyl group having 1-6 carbon atoms which does not have an acid-dissociable group, or an alkylcarbonyl group having 2-7 carbon atoms which does not have an acid-dissociable group,  $X^1$  represents a linear or branched fluoroalkyl group having 1-4 carbon atoms,  $R^2$  represents a hydrogen atom, a linear or branched alkyl group having 1-10 carbon atoms, or a linear or branched fluoroalkyl group having 1-10 carbon atoms,  $R^3$ ,  $R^4$ , and  $R^5$  individually represent a

hydrogen atom, a linear or branched alkyl group having 1-4 carbon atoms, a monovalent oxygen-containing polar group, or a monovalent nitrogen-containing polar group, n is an integer of 0-2, and m is an integer of 0-3.

[Claim 4] The radiation-sensitive resin composition according to claim 3, wherein the alkali insoluble or scarcely soluble acid-dissociating group-containing resin (A) has a recurring unit (I), recurring unit (II), and recurring unit (III) shown by the following formula (4):

[Chemical Formula 4]



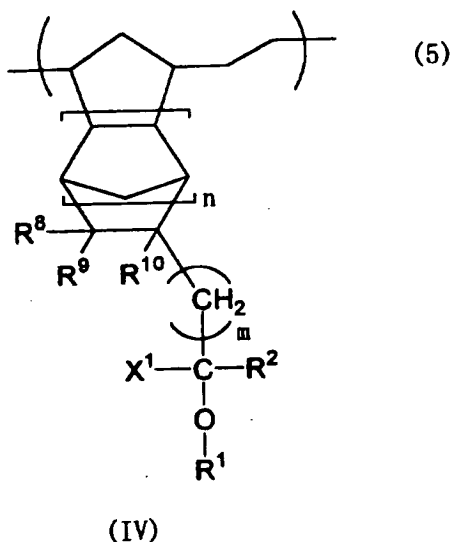
wherein R<sup>1</sup> represents a hydrogen atom, a monovalent acid-dissociable group, an alkyl group having 1-6 carbon atoms which does not have an acid-dissociable group, or an alkylcarbonyl group having 2-7 carbon atoms which does not have an acid-dissociable group, X<sup>1</sup> represents a linear or branched



fluoroalkyl group having 1-4 carbon atoms,  $R^2$  represents a hydrogen atom, a linear or branched alkyl group having 1-10 carbon atoms, or a linear or branched fluoroalkyl group having 1-10 carbon atoms,  $R^3$ ,  $R^4$ , and  $R^5$  individually represent a hydrogen atom, a linear or branched alkyl group having 1-4 carbon atoms, a monovalent oxygen-containing polar group, or a monovalent nitrogen-containing polar group,  $n$  is an integer of 0-2,  $m$  is an integer of 0-3,  $R^6$  is a hydrogen atom or a methyl group, each  $R^7$  individually represents a linear or branched alkyl group having 1-4 carbon atoms or a monovalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof, or any two of  $R^7$  groups form in combination a divalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof together with a carbon atom to which each  $R^7$  bonds, with the remaining  $R^7$  being a linear or branched alkyl group having 1-4 carbon atoms or a monovalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof.

[Claim 5] A radiation-sensitive resin composition comprising (A) an acid-dissociating group-containing resin having a structural unit (IV) represented by the following formula (5) and (B) a photoacid generator:

[Chemical Formula 5]



wherein  $R^1$  represents a hydrogen atom, a monovalent acid-dissociable group, an alkyl group having 1-6 carbon atoms which does not have an acid-dissociable group, or an alkylcarbonyl group having 2-7 carbon atoms which does not have an acid-dissociable group,  $X^1$  represents a linear or branched fluoroalkyl group having 1-4 carbon atoms,  $R^2$  represents a hydrogen atom, a linear or branched alkyl group having 1-10 carbon atoms, or a linear or branched fluoroalkyl group having 1-10 carbon atoms,  $R^8$ ,  $R^9$ , and  $R^{10}$  individually represent a hydrogen atom, a linear or branched alkyl group having 1-4 carbon atoms, a monovalent oxygen-containing polar group, or a monovalent nitrogen-containing polar group,  $n$  is an integer of 0-2, and  $m$  is an integer of 0-3.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a radiation-sensitive resin composition and, more particularly, to a radiation-sensitive resin composition suitable as a chemically-amplified resist useful for microfabrication utilizing various types of radiation, for example, deep ultraviolet rays such as a KrF excimer laser or ArF excimer laser, X-rays such as synchrotron radiation, or charged particle rays such as electron beams.

[0002]

[Prior Art]

In the field of microfabrication represented by fabrication of integrated circuit devices, lithographic technology enabling microfabrication with a line width of 0.20  $\mu\text{m}$  or less is demanded in recent years in order to achieve a higher degree of integration.

A conventional lithographic process generally utilizes near ultraviolet rays such as an i-line radiation. It is known in the art that microfabrication with a line width of sub-quarter micron using near ultraviolet rays is very difficult.

Therefore, use of radiation with a shorter wavelength has been studied for enabling microfabrication with a line width of 0.20  $\mu\text{m}$  or less. Deep ultraviolet rays represented by a line spectrum of a mercury lamp and an excimer laser, X-rays, electron beams, and the like can be given as radiation with a shorter wavelength. Of these, a KrF excimer laser (wavelength: 248 nm) and an ArF excimer laser (wavelength: 193 nm) have

attracted attention.

As a radiation-sensitive resin composition applicable to the excimer laser radiation, a number of compositions utilizing a chemical amplification effect between a component having an acid-dissociable functional group and a component generating an acid (hereinafter called "photoacid generator") upon irradiation (hereinafter called "exposure") have been proposed. Such a composition is hereinafter called a chemically-amplified radiation-sensitive composition.

As the chemically-amplified radiation-sensitive composition, Japanese Patent Publication No. 27660/1990 discloses a composition comprising a polymer containing a t-butyl ester group of carboxylic acid or a t-butylcarbonate group of phenol and a photoacid generator. This composition utilizes the effect of the polymer to release a t-butyl ester group or t-butyl carbonate group in the polymer by the action of an acid generated upon exposure to form an acidic group such as a carboxylic group or a phenolic hydroxyl group, which renders the exposed area on the resist film readily soluble in an alkaline developer.

[0003]

Most of conventional chemically-amplified radiation-sensitive compositions use a phenol resin as a base resin. Deep ultraviolet rays used as radiations for exposure are absorbed due to an aromatic ring in the resin and cannot sufficiently reach the lower layers of the resist film. Because of this, the dose of the radiation is greater in the upper layers

and is smaller in the lower layers of the resist film. This causes a resist pattern to be thinner in the upper portion but to be thicker toward the lower portion, thereby forming a trapezoid shape after development. No sufficient resolution can be obtained from such a resist film. Such a trapezoid resist pattern formed after development cannot give a desirable dimensional accuracy in the succeeding steps such as an etching step and an ion implantation step. In addition, if the configuration of the upper resist pattern is not rectangular, the resist disappears faster during dry etching, making it difficult to control etching conditions.

The shape of the resist pattern can be improved by increasing the radiation transmittance through the resist film. For example, (meth)acrylate resins represented by polymethylmethacrylate are desirable from the viewpoint of radiation transmittance due to the superior transparency to deep ultraviolet rays. Japanese Patent Application Laid-open No. 226461/1992 proposes a chemically-amplified radiation-sensitive resin composition using a methacrylate resin. However, in spite of the excellent micro-processing performance, this composition exhibits only poor dry etching resistance due to the absence of an aromatic ring, giving rise to difficulty in performing etching with high accuracy. This composition thus does not have both radiation transmittance and dry etching resistance at the same time.

[0004]

A method of introducing an alicyclic ring into the resin

component in the composition instead of an aromatic ring has been known as a means of improving dry etching resistance without impairing radiation transmittance of the resist made from a chemically-amplified radiation-sensitive resin composition. A chemically-amplified radiation-sensitive resin composition using a (meth)acrylate resin having an alicyclic ring is proposed in Japanese Patent Application Laid-open No. 234511/1995, for example.

This composition, however, comprises groups which are comparatively easily dissociated by the effect of conventional acids (for example, an acetal functional group such as a tetrahydropyranyl group) and groups which are comparatively difficult to be dissociated by the effect of acids (for example, a t-butyl functional group such as a t-butyl ester group, t-butyl carbonate group) as an acid-dissociable functional group in the resin component. The resin component possessing the former acid-dissociable functional group exhibits excellent basic characteristics as a resist such as superior sensitivity and excellent pattern shape, but has a problem of poor storage stability, whereas the resin component possessing the latter acid-dissociable functional group exhibits impaired resist characteristics, particularly in terms of sensitivity and pattern shape, in spite of excellent storage stability. In addition, inclusion of an alicyclic structure in the resin components of this composition increases hydrophobicity of the resin, resulting in poor adhesion to substrates.

In view of recent progress in the microfabrication of

semiconductor devices, development of a novel resin component exhibiting high transmittance of radiations, having excellent basic properties as a resist, and suitable for use in chemically amplified radiation sensitive compositions which can be adapted for short wavelength radiations represented by deep ultraviolet rays is an important subject.

[0005]

[Problems to be Solved by the Invention]

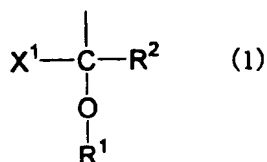
Therefore, an object of the present invention is to provide a novel radiation-sensitive resin composition, which has high transmittance of radiation, exhibits superior basic properties as a resist such as high sensitivity, resolution, and pattern shape, and is capable of producing semiconductor devices at a high yield without producing developing defects during microfabrication.

[0006]

[Means for Solving the Problems]

The above object can be achieved by the present invention by a radiation-sensitive resin composition comprising (A) an acid-dissociating group-containing resin having a structure represented by the following formula (1) and (B) a photoacid generator:

[Chemical Formula 6]



wherein  $R^1$  represents a hydrogen atom, a monovalent acid-dissociable group, an alkyl group having 1-6 carbon atoms which does not have an acid-dissociable group, or an alkylcarbonyl group having 2-7 carbon atoms which does not have an acid-dissociable group,  $X^1$  represents a linear or branched fluoroalkyl group having 1-4 carbon atoms, and  $R^2$  represents a hydrogen atom, a linear or branched alkyl group having 1-10 carbon atoms, or a linear or branched fluoroalkyl group having 1-10 carbon atoms.

[0007]

The present invention will be described in detail below.

#### Component (A)

The component (A) of the present invention is an acid-dissociating group-containing resin (hereinafter referred to as "resin (A)") represented by the above-described structure (hereinafter referred to as "structure (1)").

The radiation-sensitive resin composition of the present invention exhibits excellent solubility in a developer and produces no developing defects due to possession of the structure (1) by the resin (A).

[0008]

As examples of the monovalent acid-dissociable group represented by  $R^1$  in the formula (1) (hereinafter referred to as an "acid-dissociating group (i)"), a tertiary alkyl group, acetal group, substituted methyl group, 1-substituted ethyl group, 1-substituted propyl group, 1-branched alkyl group



(excluding tertiary alkyl groups), silyl group, germyl group, alkoxycarbonyl group, acyl group, cyclic acid-dissociable group, and the like can be given.

[0009]

As examples of the tertiary alkyl group in the acid-dissociating group (i), a t-butyl group, 1,1-dimethylpropyl group, 1-methyl-1-ethylpropyl group, 1,1-dimethylbutyl group, 1-methyl-1-ethylbutyl group, 1,1-dimethylpentyl group, 1-methyl-1-ethylpentyl group, 1,1-dimethylhexyl group, 1,1-dimethylheptyl group, 1,1-dimethyloctyl group, and the like can be given.

As examples of the acetal group, a methoxymethoxy group, ethoxymethoxy group, n-propoxymethoxy group, i-propoxymethoxy group, n-butoxymethoxy group, t-butoxymethoxy group, n-pentyloxymethoxy group, n-hexyloxymethoxy group, cyclopentyloxymethoxy group, cyclohexyloxymethoxy group, 1-methoxyethoxy group, 1-ethoxyethoxy group, 1-n-propoxyethoxy group, 1-i-propoxyethoxy group, 1-n-butoxyethoxy group, 1-t-butoxyethoxy group, 1-n-pentyloxyethoxy group, 1-n-hexyloxyethoxy group, 1-cyclopentyloxyethoxy group, 1-cyclohexyloxyethoxy group, (cyclohexyl)(methoxy)methoxy group, (cyclohexyl)(ethoxy)methoxy group, (cyclohexyl)(n-propoxy)methoxy group, (cyclohexyl)(i-propoxy)methoxy group, (cyclohexyl)(cyclohexyloxy)methoxy group, and the like can be given.

[0010]

As examples of the substituted methyl group, a methoxymethyl group, methylthiomethyl group, ethoxymethyl group, ethylthiomethyl group, methoxyethoxymethyl group, benzyloxymethyl group, benzylthiomethyl group, phenacyl group, bromophenacyl group, methoxyphenacyl group, methylthiophenacyl group,  $\alpha$ -methylphenacyl group, cyclopropylmethyl group, benzyl group, diphenylmethyl group, triphenylmethyl group, bromobenzyl group, nitrobenzyl group, methoxybenzyl group, methylthiobenzyl group, ethoxybenzyl group, ethylthiobenzyl group, piperonyl group, methoxycarbonylmethyl group, ethoxycarbonylmethyl group, n-propoxycarbonylmethyl group, i-propoxycarbonylmethyl group, n-butoxycarbonylmethyl group, t-butoxycarbonylmethyl group, and the like can be given.

As examples of the 1-substituted ethyl group, a 1-methoxyethyl group, 1-methylthioethyl group, 1,1-dimethoxyethyl group, 1-ethoxyethyl group, 1-ethylthioethyl group, 1,1-diethoxyethyl group, 1-phenoxyethyl group, 1-phenylthioethyl group, 1,1-diphenoxyethyl group, 1-benzyloxyethyl group, 1-benzylthioethyl group, 1-cyclopropylethyl group, 1-phenylethyl group, 1,1-diphenylethyl group, 1-methoxycarbonylethyl group, 1-ethoxycarbonylethyl group, 1-n-propoxycarbonylethyl group, 1-i-propoxycarbonylethyl group, 1-n-butoxycarbonylethyl group, 1-t-butoxycarbonylethyl group, and the like can be given.

As examples of the 1-substituted propyl group, a 1-methoxypropyl group, 1-ethoxypropyl group, and the like can be given.

[0011]

As examples of the 1-branched alkyl group, i-propyl group, sec-butyl group, 1-methylbutyl group, and the like can be given.

As examples of the silyl group, a trimethylsilyl group, ethyldimethylsilyl group, methyldiethylsilyl group, triethylsilyl group, i-propyldimethylsilyl group, methyldi-i-propylsilyl group, tri-i-propylsilyl group, t-butyldimethylsilyl group, methyldi-t-butylsilyl group, tri-t-butylsilyl group, phenyldimethylsilyl group, methyldiphenylsilyl group, triphenylsilyl group, and the like can be given.

As examples of the germyl group, a trimethylgermyl group, ethyldimethylgermyl group, methyldiethylgermyl group, triethylgermyl group, i-propyldimethylgermyl group, methyldi-i-propylgermyl group, tri-i-propylgermyl group, t-butyldimethylgermyl group, methyldi-t-butylgermyl group, tri-t-butylgermyl group, phenyldimethylgermyl group, methyldiphenylgermyl group, triphenylgermyl group, and the like can be given.

As examples of the alkoxycarbonyl group, a methoxycarbonyl group, ethoxycarbonyl group, i-propoxycarbonyl group, t-butoxycarbonyl group, and the like can be given.

[0012]

As examples of the acyl group, an acetyl group, propionyl

group, butyryl group, heptanoyl group, hexanoyl group, valeryl group, pivaloyl group, isovaleryl group, lauryloyl group, myristoyl group, palmitoyl group, stearoyl group, oxalyl group, malonyl group, succinyl group, glutaryl group, adipoyl group, piperoyl group, suberoyl group, azelaoyl group, sebacoyl group, acryloyl group, propioloyl group, methacryloyl group, crotonoyl group, oleoyl group, maleoyl group, fumaroyl group, mesaconoyl group, campholoyl group, benzoyl group, phthaloyl group, isophthaloyl group, terephthaloyl group, naphthoyl group, toluoyl group, hydroatropoyl group, atropoyl group, cinnamoyl group, furoyl group, thenoyl group, nicotinoyl group, isonicotinoyl group, p-toluenesulfonyl group, mesyl group, and the like can be given.

As examples of the cyclic acid-dissociable group, a 3-oxocyclohexyl group, tetrahydropyranyl group, tetrahydrofuranyl group, tetrahydrothiopyranyl group, tetrahydrothiofuranyl group, 3-bromotetrahydropyranyl group, 4-methoxytetrahydropyranyl group, 2-oxo-4-methyl-4-tetrahydropyranyl group, 4-methoxytetrahydrothiopyranyl group, 3-tetrahydrothiophene-1,1-dioxide group, and the like can be given.

[0013]

Of these acid-dissociable groups (i), a t-butyl group, 1-methoxyethoxy group, 1-ethoxyethoxy group, 1-cyclohexyloxyethoxy group, methoxymethyl group, t-butoxycarbonylmethyl group, 1-methoxyethyl group,

1-ethoxyethyl group, 1-n-propoxyethyl group,  
1-cyclohexyloxyethyl group, 1-ethoxypropyl group,  
trimethylsilyl group, t-butoxycarbonyl group,  
tetrahydropyranyl group, tetrahydrofuranyl group, and the like  
are preferable.

[0014]

The alkyl group having 1-6 carbon atoms having no  
acid-dissociating group represented by  $R^1$  may be linear,  
branched or cyclic, and the examples include a methyl group,  
ethyl group, n-propyl group, n-butyl group, i-butyl group,  
n-pentyl group, n-hexyl group, cyclopentyl group, and  
cyclohexyl group.

Of these alkyl groups, a methyl group, ethyl group,  
n-propyl group, cyclohexyl group, and the like are particularly  
preferable.

[0015]

The alkylcarbonyl group having 2-7 carbon atoms having no  
acid-dissociating group represented by  $R^1$  may be linear,  
branched, or cyclic, and the examples include a methylcarbonyl  
group, ethylcarbonyl group, n-propylcarbonyl group,  
n-butylcarbonyl group, i-butylcarbonyl group,  
n-pentylcarbonyl group, i-pentylcarbonyl group,  
n-hexylcarbonyl group, i-hexylcarbonyl group, and  
cyclohexylcarbonyl group.

Of these alkylcarbonyl groups, a methylcarbonyl group,  
ethylcarbonyl group, and the like are particularly preferable.

[0016]

Particularly preferable groups for  $R^1$  in the formula (1) are a hydrogen atom, the above-mentioned preferable acid-dissociable groups (i), a methyl group, ethyl group, methylcarbonyl group, ethylcarbonyl group, and the like.

[0017]

Given as examples of the linear or the branched fluoroalkyl group having 1-4 carbon atoms represented by  $X^1$  are a fluoromethyl group, difluoromethyl group, perfluoromethyl group, 1-fluoroethyl group, 1,1-difluoroethyl group, 2,2,2-trifluoroethyl group, perfluoroethyl group, 1-fluoro-n-propyl group, 1,1-difluoro-n-propyl group, 3,3,3-trifluoro-n-propyl group, 3,3,3,2,2-pentafluoro-n-propyl group, perfluoro-n-propyl group, 1-fluoro-1-methylethyl group, 2,2,2-trifluoro-1-methylethyl group, perfluoro-i-propyl group, 1-fluoro-n-butyl group, 1,1-difluoro-n-butyl group, 4,4,4-trifluoro-n-butyl group, 4,4,4,3,3-pentafluoro-n-butyl group, 4,4,4,3,3,2,2-heptafluoro-n-butyl group, perfluoro-n-butyl group, and the like.

Of these fluoroalkyl groups, a fluoromethyl group, difluoromethyl group, perfluoromethyl group, 1,1-difluoroethyl group, 2,2,2-trifluoroethyl group, 1-fluoro-1-methylethyl group, and the like are preferable.

[0018]

Given as examples of the linear or the branched alkyl group having 1-10 carbon atoms represented by  $R^2$  are a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group,

i-butyl group, sec-butyl group, t-butyl group, n-pentyl group, neopentyl group, n-hexyl group, n-heptyl group, n-octyl group, 2-ethylhexyl group, n-nonyl group, n-decyl group, and the like.

Of these, a methyl group, ethyl group, n-propyl group, n-hexyl group, and the like are preferable.

[0019]

Given as examples of the linear or the branched fluoroalkyl group having 1-10 carbon atoms represented by  $R^2$  are a fluoromethyl group, difluoromethyl group, perfluoromethyl group, 1-fluoroethyl group, 1,1-difluoroethyl group, 2,2,2-trifluoroethyl group, perfluoroethyl group, 1-fluoro-n-propyl group, 1,1-difluoro-n-propyl group, 3,3,3-trifluoro-n-propyl group, 3,3,3,2,2-pentafluoro-n-propyl group, perfluoro-n-propyl group, 1-fluoro-1-methylethyl group, 2-trifluoro-1-methylethyl group, perfluoro-i-propyl group, 1-fluoro-n-butyl group, 1,1-difluoro-n-butyl group, 4,4,4-trifluoro-n-butyl group, 4,4,4,3,3-pentafluoro-n-butyl group, 4,4,4,3,3,2,2-heptafluoro-n-butyl group, perfluoro-n-butyl group, 2-fluoro-2-methylpropyl group, 1-fluoro-1-methylpropyl group, 1-fluoro-n-pentyl group, 1,1-difluoro-n-pentyl group, 5,5,5-trifluoro-n-pentyl group, 1-fluoro-n-hexyl group, 1,1-difluoro-n-hexyl group, 6,6,6-trifluoro-n-hexyl group, 1-fluoro-n-heptyl group, 1,1-difluoro-n-heptyl group, 7,7,7-trifluoro-n-heptyl group, 1-fluoro-n-octyl group, 1,1-difluoro-n-octyl group, 8,8,8-trifluoro-n-octyl group, 2-fluoro-2-ethylhexyl group,

1-fluoro-n-nonyl group, 1,1-difluoro-n-nonyl group,  
 9,9,9-trifluoro-n-nonyl group, 1-fluoro-n-decyl group,  
 1,1-difluoro-n-decyl group, 10,10,10-trifluoro-n-decyl group,  
 and the like.

Of these fluoroalkyl groups, a fluoromethyl group,  
 difluoromethyl group, perfluoromethyl group,  
 1,1-difluoroethyl group, 2,2,2-trifluoroethyl group,  
 1-fluoro-1-methylethyl group, and the like are preferable.

[0020]

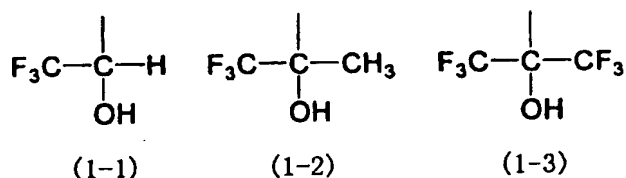
Particularly preferable groups for R<sup>2</sup> in the formula (2)  
 are a hydrogen atom, methyl group, perfluoromethyl group, and  
 the like.

[0021]

Specific preferable examples of the structure (1) include  
 the structures of the following formulas (1-1) to (1-12).

[0022]

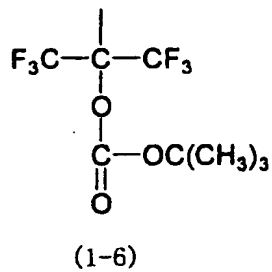
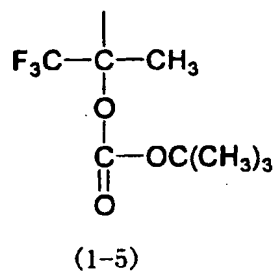
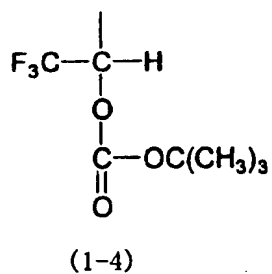
[Chemical Formula 7]



[0023]

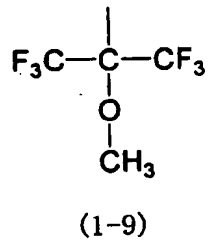
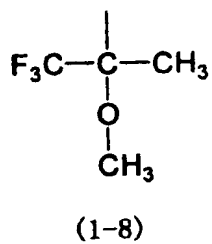
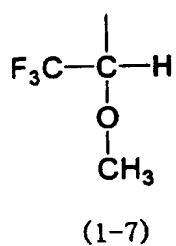
[Chemical Formula 8]





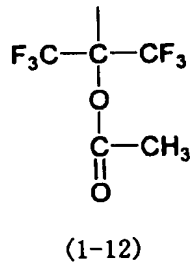
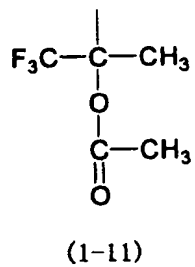
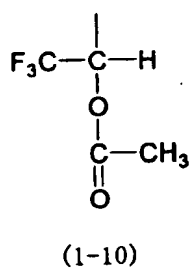
[0024]

[Chemical Formula 9]



[0025]

[Chemical Formula 10]



[0026]

Of these, the structures shown by the formulas (1-3), (1-6), (1-12), and the like are preferable.

[0027]

Any resins including addition condensation resins, polyaddition resins, ring-opening polymerization resins, condensation polymerization resins, and the like can be employed without specific limitations as the resin (A) inasmuch as the resin has an acid-dissociating group possessing the structure (1). From the viewpoint of transmittance of radioactive rays, the resin (A) of the present invention preferably does not have an aromatic ring or contains as small an amount of aromatic rings as possible.

As preferable specific examples of the resin (A) in the present invention, an acid-dissociating group-containing resin having a recurring unit (I) shown by the following formula (2) (hereinafter referred to as "resin (A1)"), an acid-dissociating group-containing resin having a recurring unit (IV) shown by the following formula (5) (hereinafter referred to as "resin (A2)"), and the like can be given.

[0028]

[Chemical Formula 11]



[ 0029 ]

23



group represented by  $R^3$ ,  $R^4$ , or  $R^5$ , a hydroxyl group; carboxyl group; linear or branched hydroxyalkyl groups having 1-4 carbon atoms such as a hydroxymethyl group, 1-hydroxyethyl group, 2-hydroxyethyl group, 1-hydroxy-n-propyl group, 2-hydroxy-n-propyl group, 3-hydroxy-n-propyl group, 1-hydroxy-n-butyl group, 2-hydroxy-n-butyl group, 3-hydroxy-n-butyl group, and 4-hydroxy-n-butyl group; linear or branched alkoxy groups having 1-4 carbon atoms such as a methoxy group, ethoxy group, n-propoxy group, i-propoxy group, n-butoxy group, 2-methylpropoxy group, 1-methylpropoxy group, and t-butoxy group; and the like can be given.

Of these oxygen-containing polar groups, a hydroxyl group, carboxyl group, hydroxymethyl group, methoxy group, ethoxy group, and the like are preferable.

[0032]

As examples of the monovalent nitrogen-containing polar group represented by  $R^3$ ,  $R^4$ , or  $R^5$ , a cyano group; linear or branched cyanoalkyl groups having 2-5 carbon atoms such as a cyanomethyl group, 1-cyanoethyl group, 2-cyanoethyl group, 1-cyano-n-propyl group, 2-cyano-n-propyl group, 3-cyano-n-propyl group, 1-cyano-n-butyl group, 2-cyano-n-butyl group, 3-cyano-n-butyl group, 4-cyano-n-butyl group; and the like can be given.

Of these nitrogen-containing polar groups, a cyano group, cyanomethyl group, 1-cyanoethyl group, and the like are preferable.

[0033]

Particularly preferable groups represented by  $R^3$ ,  $R^4$ , or  $R^5$  in the formulas (2) are a hydrogen atom, methyl group, ethyl group, hydroxyl group, carboxyl group, hydroxymethyl group, methoxy group, ethoxy group, cyano group, cyanomethyl group, 1-cyanoethyl group, and the like.

m and n in the formula (2) are preferably either 0 or 1.

The recurring unit (I) may be present in the resin (A1) either individually or in combination of two or more.

[0034]

As preferable examples of the resin (A1) in the present invention, an alkali insoluble or scarcely alkali soluble acid-dissociating group-containing resin having the recurring unit (I) and recurring unit (II) shown by the following formula (3) (hereinafter referred to as "resin (A1-1)"), an alkali insoluble or scarcely alkali soluble acid-dissociating group-containing resin having the recurring unit (I), recurring unit (II), and recurring unit (III) shown by the following formula (4) (hereinafter referred to as "resin (A1-2)"), and the like can be given.

[0035]

[Chemical Formula 13]



[0036]

$$\begin{array}{ccc}
 \text{(I)} & \text{(II)} & \text{(III)} \\
 \left( \begin{array}{c} \text{HC} - \text{CH} \\ | \quad | \\ \diagdown \quad / \\ | \quad | \\ \diagup \quad \diagdown \\ | \quad | \\ \diagdown \quad / \\ | \quad | \\ \diagup \quad \diagdown \\ | \quad | \\ \text{R}^3 \quad \text{R}^4 \quad \text{R}^5 \end{array} \right)_n & \left( \begin{array}{c} \text{O}=\text{C}-\text{O}-\text{C}=\text{O} \\ | \quad | \\ \text{HC} - \text{CH} \end{array} \right) & \begin{array}{c} \text{R}^6 \\ | \\ \left( \text{C} - \text{CH}_2 \right) \\ | \\ \text{O}=\text{C} \\ | \\ \text{O} \\ | \\ \text{R}^7 - \text{C} - \text{R}^7 \\ | \\ \text{R}^7 \end{array}
 \end{array}$$

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wherein  $R^1$ ,  $X^1$ , and  $R^2$  are the same as defined in the above formula (1),  $R^3$ ,  $R^4$ ,  $R^5$ ,  $n$ , and  $m$  are the same as defined in the above formula (2),  $R^6$  represents a hydrogen atom or methyl group,  $R^7$  individually represents a linear or branched alkyl group having 1-4 carbon atoms or a monovalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof, or any two of  $R^7$  groups form in combination a divalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof together with a carbon atom to which each  $R^7$  bonds, with the remaining  $R^7$  group being a linear or branched alkyl group having 1-4 carbon atoms or a monovalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof.

[0037]

As examples of the linear or branched alkyl group having 1-4 carbon atoms represented by  $R^7$  in the formula (4), a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, 2-methylpropyl group, 1-methylpropyl group, t-butyl group, and the like can be given.

Of these alkyl groups, a methyl group, ethyl group, and the like are particularly preferable.

[0038]

As examples of the monovalent alicyclic hydrocarbon group having 4-20 carbon atoms represented by  $R^7$  and the divalent alicyclic hydrocarbon group having 4-20 carbon atoms formed by two  $R^7$ s in combination, alicyclic groups derived from cycloalkanes such as norbornane, tricyclodecane, tetracyclododecane, adamantane, cyclobutane, cyclopentane,



cyclohexane, cycloheptane, or cyclooctane, and groups obtained by replacing hydrogen atoms on these alicyclic groups with one or more linear or branched alkyl groups having 1-4 carbon atoms, such as a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, 2-methyl propyl group, 1-methyl propyl group, or t-butyl group, can be given.

Of these monovalent and divalent alicyclic hydrocarbon groups, groups containing an alicyclic ring derived from norbornane, tricyclodecane, tetracyclododecane, or adamantane, groups in which these alicyclic ring-containing groups are substituted with the above alkyl groups, and the like are preferable.

[0039]

As examples of derivatives of the monovalent or divalent alicyclic hydrocarbon groups, groups having one or more substituents such as a hydroxyl group; a carboxyl group; a linear or branched hydroxyalkyl group having 1-4 carbon atoms such as a hydroxymethyl group, 1-hydroxyethyl group, 2-hydroxyethyl group, 1-hydroxy-n-propyl group, 2-hydroxy-n-propyl group, 3-hydroxy-n-propyl group, 1-hydroxy-n-butyl group, 2-hydroxy-n-butyl group, 3-hydroxy-n-butyl group, and 4-hydroxy-n-butyl group; a linear or branched alkoxy group having 1-4 carbon atoms such as a methoxy group, ethoxy group, n-propoxy group, i-propoxy group, n-butoxy group, 2-methylpropoxy group, 1-methylpropoxy group, and t-butoxy group; a cyano group; a linear or branched cyanoalkyl group having 2-5 carbon atoms such as a cyanomethyl

group, 1-cyanoethyl group, 2-cyanoethyl group, 1-cyanopropyl group, 2-cyanopropyl group, 3-cyanopropyl group, 1-cyanobutyl group, 2-cyanobutyl group, 3-cyanobutyl group, and 4-cyanobutyl group; and the like can be given.

Of these substituents, a hydroxyl group, carboxyl group, hydroxymethyl group, cyano group, cyanomethyl group, and the like are preferable.

[0040]

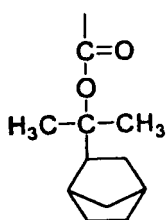
The group  $-\text{COO}-\text{C}(\text{R}^7)_3$  in the recurring unit (III) in the formula (4) dissociates at the carbonyloxy group ( $\text{COO}-$ ) and the group  $-\text{C}(\text{R}^7)_3$  in the presence of an acid, and is herein called acid-dissociating group (ii).

[0041]

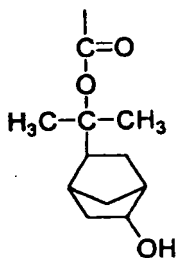
Specific preferable examples of the acid-dissociating group (ii) include a t-butoxycarbonyl group and the groups shown by the following formulas (ii-1) to (ii-57).

[0042]

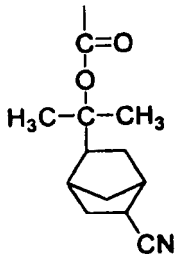
[Chemical Formula 15]



(ii-1)



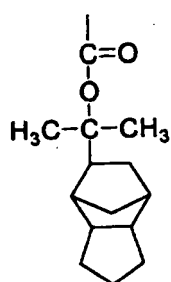
(ii-2)



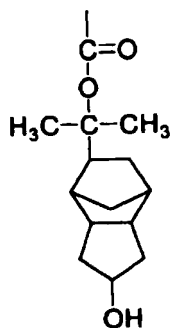
(ii-3)

[0043]

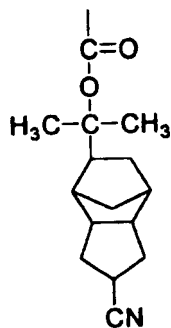
[Chemical Formula 16]



(ii-4)



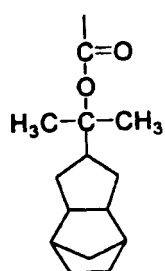
(ii-5)



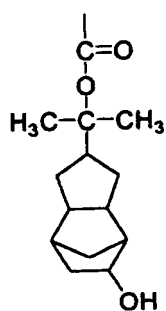
(ii-6)

[0044]

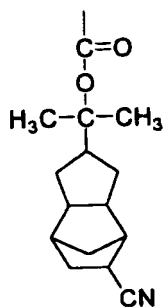
[Chemical Formula 17]



(ii-7)



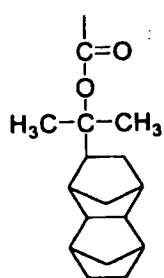
(ii-8)



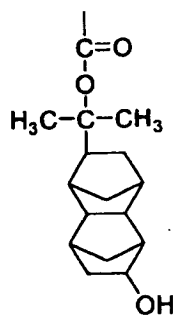
(ii-9)

[0045]

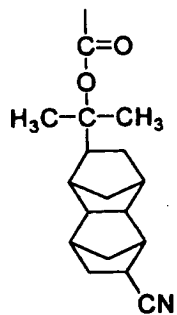
[Chemical Formula 18]



(ii-10)



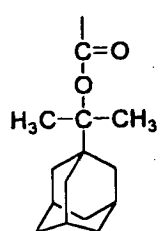
(ii-11)



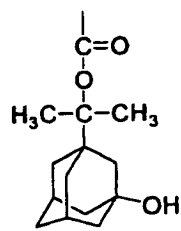
(ii-12)

[0046]

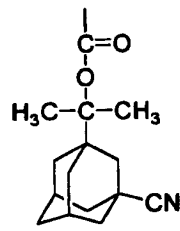
[Chemical Formula 19]



(ii-13)



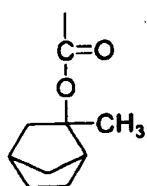
(ii-14)



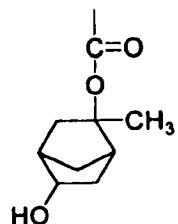
(ii-15)

[0047]

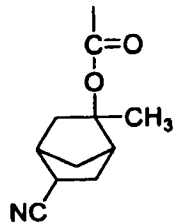
[Chemical Formula 20]



(ii-16)



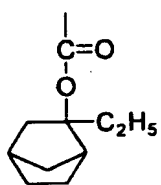
(ii-17)



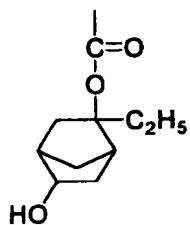
(ii-18)

[0048]

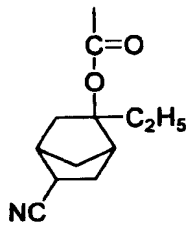
[Chemical Formula 21]



(ii-19)



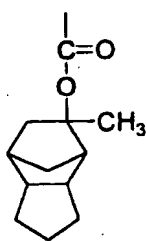
(ii-20)



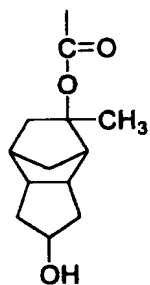
(ii-21)

[0049]

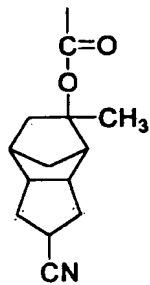
[Chemical Formula 22]



(ii-22)



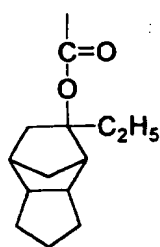
(ii-23)



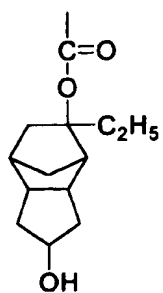
(ii-24)

[0050]

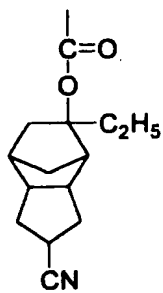
[Chemical Formula 23]



(ii-25)



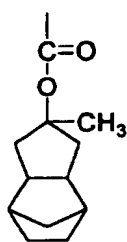
(ii-26)



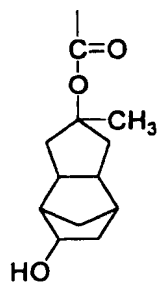
(ii-27)

[0051]

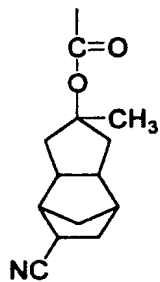
[Chemical Formula 24]



(ii-28)



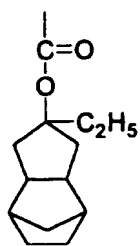
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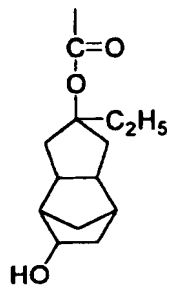
(ii-30)

[0052]

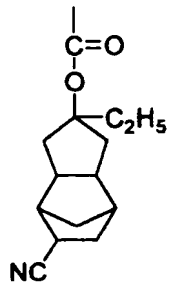
[Chemical Formula 25]



(ii-31)



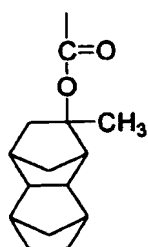
(ii-32)



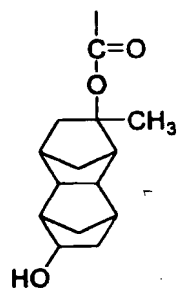
(ii-33)

[0053]

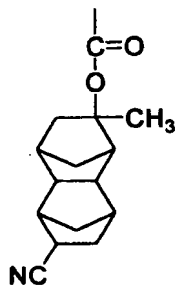
[Chemical Formula 26]



(ii-34)



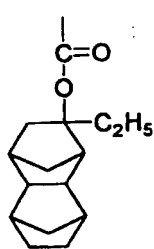
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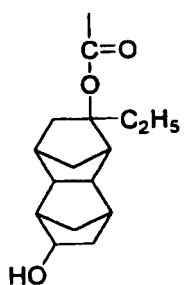
(ii-36)

[0054]

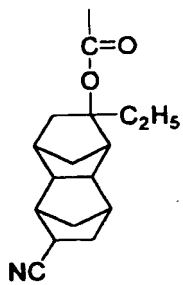
[Chemical Formula 27]



(ii-37)



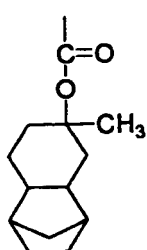
(ii-38)



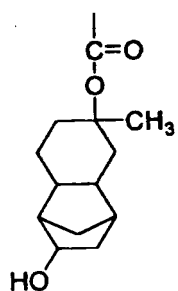
(ii-39)

[0055]

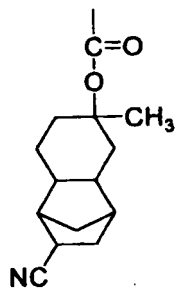
[Chemical Formula 28]



(ii-40)



(ii-41)

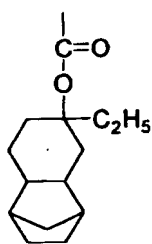


(ii-42)

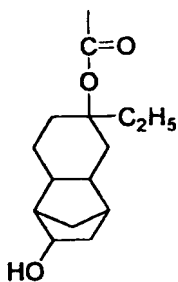
[0056]

[Chemical Formula 29]

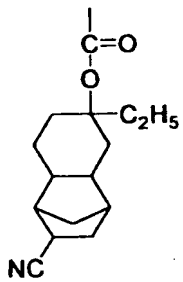




(ii-43)



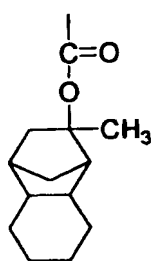
(ii-44)



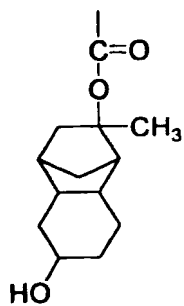
(ii-45)

[0057]

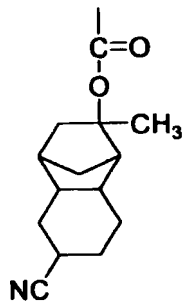
[Chemical Formula 30]



(ii-46)



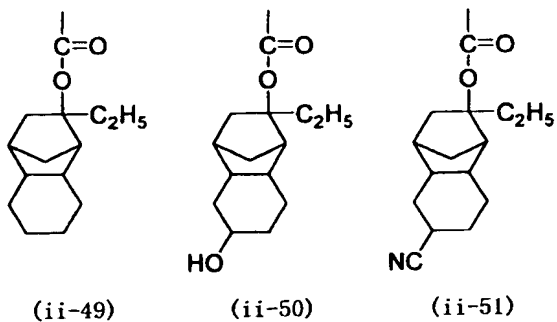
(ii-47)



(ii-48)

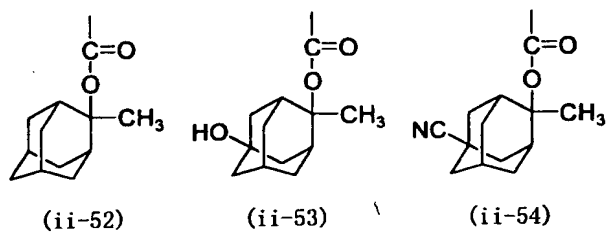
[0058]

[Chemical Formula 31]



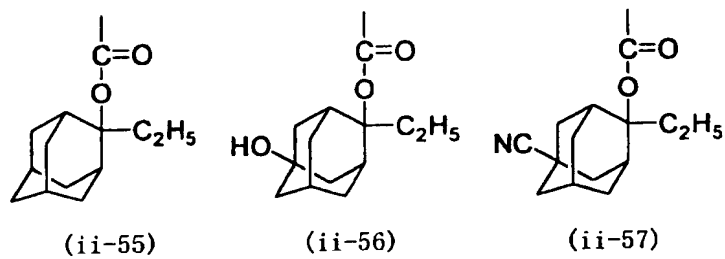
[0059]

[Chemical Formula 32]



[0060]

[Chemical Formula 33]



[0061]

Of these acid-dissociating groups (ii), t-butoxy carbonyl

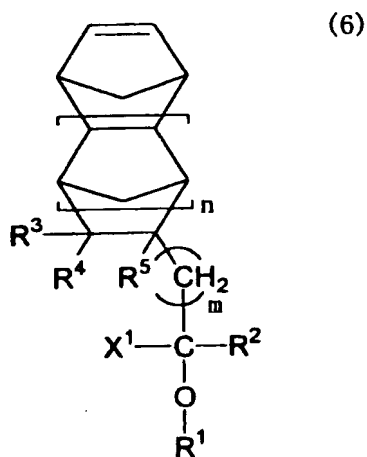
group, 1-methylcyclopentyloxycarbonyl group, 1-methylcyclohexyloxycarbonyl group, the groups shown by the formulas (ii-1), (ii-2), (ii-10), (ii-11), (ii-13), (ii-14), (ii-16), (ii-17), (ii-22), (ii-23), (ii-34), (ii-35), (ii-40), (ii-41), (ii-52), and (ii-53), and the like are particularly preferable.

[0062]

As examples of monomers which provide the recurring unit (I) in the resin (A1), resin (A1-1), and resin (A1-2), compounds shown by the following formula (6) (hereinafter referred to as "norbornene derivatives ( $\alpha 1$ )") can be given:

[0063]

[Chemical Formula 34]



[0064]

wherein  $R^1$ ,  $X^1$ , and  $R^2$  are the same as defined in the above formula (1), and  $R^3$ ,  $R^4$ ,  $R^5$ ,  $n$ , and  $m$  are the same as defined in the above formula (2).

[0065]

The following compounds can be given as examples of the norbornene derivatives ( $\alpha 1$ ) having  $n=m=0$  in the formula (6):

5-(2,2,2-trifluoro-1-hydroxyethyl)bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-methyl-1-hydroxyethyl)bicyclo[2.2.1]

hept-2-ene,

5-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)

bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-methoxyethyl)bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-methyl-1-methoxyethyl)bicyclo[2.2.1]

hept-2-ene,

5-(2,2,2-trifluoro-1-trifluoromethyl-1-methoxyethyl)

bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-methylcarbonyloxyethyl)bicyclo[2.2.1]

hept-2-ene,

5-(2,2,2-trifluoro-1-methyl-1-methylcarbonyloxyethyl)

bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-trifluoromethyl-1-

methylcarbonyloxyethyl)bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-t-butoxycarbonyloxyethyl)bicyclo

[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-methyl-1-t-butoxycarbonyloxyethyl)

bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-trifluoromethyl-1-t-

butoxycarbonyloxyethyl)bicyclo[2.2.1]hept-2-ene, and the

like.

[0066]

The following compounds can be given as examples of the norbornene derivatives ( $\alpha 1$ ) having  $n=0$  and  $m=1$  in the formula (6):

5-(2-trifluoromethyl-2-hydroxyethyl)bicyclo[2.2.1]hept-2-ene, 5-(2-trifluoromethyl-2-methyl-2-hydroxyethyl)bicyclo[2.2.1]hept-2-ene,  
 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene, 5-(2-trifluoromethyl-2-methoxyethyl)bicyclo[2.2.1]hept-2-ene,  
 5-(2-trifluoromethyl-2-methyl-2-methoxyethyl)bicyclo[2.2.1]hept-2-ene,  
 5-[2,2-bis(trifluoromethyl)-2-methoxyethyl]bicyclo[2.2.1]hept-2-ene,  
 5-[2-trifluoromethyl-2-methylcarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene, 5-(2-trifluoromethyl-2-methyl-2-methylcarbonyloxyethyl)bicyclo[2.2.1]hept-2-ene,  
 5-[2,2-bis(trifluoromethyl)-2-methylcarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene,  
 5-[2-trifluoromethyl-2-t-butoxycarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene,  
 5-(2-trifluoromethyl-2-methyl-2-t-butoxycarbonyloxyethyl)bicyclo[2.2.1]hept-2-ene,  
 5-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene.

[0067]

The following compounds can be given as examples of the norbornene derivatives ( $\alpha 1$ ) having  $n=1$  and  $m=0$  in the formula

(6) :

8-(2,2,2-trifluoro-1-hydroxyethyl) tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2,2,2-trifluoro-1-methyl-1-hydroxyethyl) tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)  
tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2,2,2-trifluoro-1-methoxyethyl) tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2,2,2-trifluoro-1-methyl-1-methoxyethyl) tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2,2,2-trifluoro-1-trifluoromethyl-1-methoxyethyl)  
tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2,2,2-trifluoro-1-methylcarbonyloxyethyl) tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2,2,2-trifluoro-1-methyl-1-methylcarbonyloxyethyl)  
tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2,2,2-trifluoro-1-trifluoromethyl-1-  
methylcarbonyloxyethyl) tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]  
dodec-3-ene,  
8-(2,2,2-trifluoro-1-t-butoxycarbonyloxyethyl) tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2,2,2-trifluoro-1-methyl-1-t-butoxycarbonyloxyethyl)  
tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2,2,2-trifluoro-1-trifluoromethyl-1-t-  
butoxycarbonyloxyethyl) tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]  
dodec-3-ene, and the like.

[0068]

The following compounds can be given as examples of the norbornene derivatives ( $\alpha 1$ ) having  $n=1$  and  $m=1$  in the formula (6):

8-(2-trifluoromethyl-2-hydroxyethyl)tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2-trifluoromethyl-2-methyl-2-hydroxyethyl)tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2-trifluoromethyl-2-methoxyethyl)tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2-trifluoromethyl-2-methyl-2-methoxyethyl)tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-[2,2-bis(trifluoromethyl)-2-methoxyethyl]tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-[2-trifluoromethyl-2-methylcarbonyloxyethyl]tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2-trifluoromethyl-2-methyl-2-methylcarbonyloxyethyl)  
tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-[2,2-bis(trifluoromethyl)-2-methylcarbonyloxyethyl]  
tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-[2-trifluoromethyl-2-t-butoxycarbonyloxyethyl]tetracyclo  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2-trifluoromethyl-2-methyl-2-t-butoxycarbonyloxyethyl)  
tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]

tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, and the like.

[0069]

Of these norbornene derivatives ( $\alpha 1$ ), the following compounds are preferable:

5-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)  
bicyclo[2.2.1]hept-2-ene,  
5-(2,2,2-trifluoro-1-trifluoromethyl-1-methoxyethyl)  
bicyclo[2.2.1]hept-2-ene,  
5-(2,2,2-trifluoro-1-trifluoromethyl-1-  
methylcarbonyloxyethyl)bicyclo[2.2.1]hept-2-ene,  
5-(2,2,2-trifluoro-1-trifluoromethyl-1-t-  
butoxycarbonyloxy ethyl)bicyclo[2.2.1]hept-2-ene,  
5-(2,2-bis(trifluoromethyl)-2-  
hydroxyethyl)bicyclo[2.2.1]hept-2-ene,  
5-(2,2-bis(trifluoromethyl)-2-methoxyethyl)bicyclo[2.2.1]  
hept-2-ene,  
5-(2,2-bis(trifluoromethyl)-2-methylcarbonyloxyethyl)  
bicyclo[2.2.1]hept-2-ene,  
5-(2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl)  
bicyclo[2.2.1]hept-2-ene,

[0070]

8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)  
tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2,2,2-trifluoro-1-trifluoromethyl-1-methoxyethyl)  
tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8-(2,2,2-trifluoro-1-trifluoromethyl-1-  
methylcarbonyloxyethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]



dodec-3-ene,

8-(2,2,2-trifluoro-1-trifluoromethyl-1-t-butoxycarbonyloxyethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

8-{2,2-bis(trifluoromethyl)-2-hydroxyethyl}tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

8-{2,2-bis(trifluoromethyl)-2-methoxyethyl}tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

8-{2,2-bis(trifluoromethyl)-2-methylcarbonyloxyethyl}tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

8-{2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl}tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, and the like.

The norbornene derivatives ( $\alpha$ 1) can be synthesized by the method disclosed by Hiroshi Ito et al. in The American Chemical Society Symposium (1998) (see Preprint, pages 208-211).

[0071]

The monomer providing the recurring unit (II) in the resin (A1-1) and resin (A1-2) is maleic anhydride. Maleic anhydride copolymerizes well with norbornene derivatives ( $\alpha$ 1), later described norbornenes and norbornene derivatives ( $\beta$ -1), and other norbornene derivatives. The copolymerization with maleic anhydride increases the molecular weight of the resulting resin (A1-1) and resin (A1-2) to a desired level.

The monomer providing the recurring unit (III) in the resin (A1-2) is a compound derived from (meth)acrylic acid by converting the carboxyl group into the acid-dissociating group (ii).

The recurring unit (III) may be present in the resin (A1-2)

either individually or in combination of two or more.

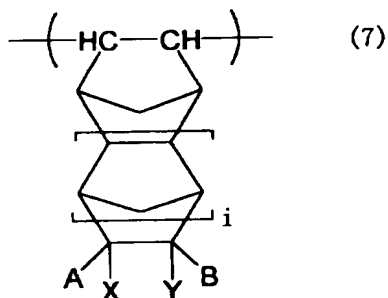
[0072]

The resin (A1), resin (A1-1), and resin (A1-2) may comprise at least one recurring unit other than the recurring units (I), (II), or (III) (hereinafter referred to as "other recurring units (a)").

As an example of the other recurring unit (a), the recurring unit containing an acid-dissociating group shown by the following formula (7) (hereinafter referred to as "recurring unit (7)") can be given.

[0073]

[Chemical Formula 35]



wherein A and B individually represent a hydrogen atom or an acid-dissociating group having 20 or less carbon atoms which dissociates and produces an acidic functional group in the presence of an acid, at least one of A and B being the acid-dissociating group, X and Y individually represent a hydrogen atom or a linear or branched monovalent alkyl group having 1-4 carbon atoms, and i is an integer of 0 to 2.

[0074]

In addition to the above acid-dissociating group (ii), the following groups can be given as examples of the acid-dissociating group represented by A or B in the formula (7):

a linear, branched, or cyclic alkoxy carbonyl group such as a methoxy carbonyl group, ethoxy carbonyl group, n-propoxy carbonyl group, i-propoxy carbonyl group, n-butoxy carbonyl group, 2-methylpropoxy carbonyl group, 1-methylpropoxy carbonyl group, n-pentyloxy carbonyl group, n-hexyloxy carbonyl group, n-heptyloxy carbonyl group, n-octyloxy carbonyl group, n-decyloxy carbonyl group, cyclopentyloxy carbonyl group, cyclohexyloxy carbonyl group, 4-t-butylcyclohexyloxy carbonyl group, cycloheptyloxy carbonyl group, and cyclooctyloxy carbonyl group;

an aryloxy carbonyl group such as a phenoxy carbonyl group, 4-t-butylphenoxy carbonyl group, and 1-naphthyloxy carbonyl group;

an aralkyloxy carbonyl group such as a benzyloxy carbonyl group, 4-t-butylbenzyloxy carbonyl group, phenethyloxy carbonyl group, and 4-t-butylphenethyloxy carbonyl group;

[0075]

a linear, branched, or cyclic 1-alkoxyethoxy carbonyl group such as a 1-methoxyethoxy carbonyl group, 1-ethoxyethoxy carbonyl group, 1-n-propoxyethoxy carbonyl group, 1-i-propoxyethoxy carbonyl group, 1-n-butoxyethoxy carbonyl group,

1-(2'-methylpropoxy)ethoxycarbonyl group,  
 1-(1'-methylpropoxy)ethoxycarbonyl group,  
 1-t-butoxyethoxycarbonyl group,  
 1-cyclohexyloxyethoxycarbonyl group, and  
 1-(4'-t-butylcyclohexyloxy)ethoxycarbonyl group;  
 a 1-aryloxyethoxycarbonyl group such as a  
 1-phenoxyethoxycarbonyl group,  
 1-(4'-t-butylphenoxy)ethoxycarbonyl group, and  
 1-(1'-naphthyloxy)ethoxycarbonyl group;  
 a 1-aralkyloxyethoxycarbonyl group such as a  
 1-benzyloxyethoxycarbonyl group,  
 1-(4'-t-butylbenzyloxy)ethoxycarbonyl group,  
 1-phenethyloxyethoxycarbonyl group, and  
 1-(4'-t-butylphenethyloxy)ethoxycarbonyl group;

[0076]

a linear, branched, or cyclic alkoxycarbonylmethoxycarbonyl  
 group such as a methoxycarbonylmethoxycarbonyl group,  
 ethoxycarbonylmethoxycarbonyl group,  
 n-propoxycarbonylmethoxycarbonyl group,  
 i-propoxycarbonylmethoxycarbonyl group,  
 n-butoxycarbonylmethoxycarbonyl group,  
 2-methylpropoxycarbonylmethoxycarbonyl group,  
 1-methylpropoxycarbonylmethoxycarbonyl group,  
 t-butoxycarbonylmethoxycarbonyl group,  
 cyclohexyloxy carbonylmethoxycarbonyl group, and  
 4-t-butylcyclohexyloxy carbonylmethoxycarbonyl group;  
 linear, branched, or cyclic alkoxycarbonylmethyl groups such

as a methoxycarbonylmethyl group, ethoxycarbonylmethyl group, n-propoxycarbonylmethyl group, i-propoxycarbonylmethyl group, n-butoxycarbonylmethyl group, 2-methylpropoxycarbonylmethyl group, 1-methylpropoxycarbonylmethyl group, t-butoxycarbonylmethyl group, cyclohexyloxycarbonylmethyl group, and 4-t-butylcyclohexyloxycarbonylmethyl group; an aryloxycarbonylmethyl group such as a phenoxycarbonylmethyl group, 4-t-butylphenoxycarbonylmethyl group, and 1-naphthyloxycarbonylmethyl group; an aralkyloxycarbonylmethyl group such as a benzyloxycarbonylmethyl group, 4-t-butylbenzyloxycarbonylmethyl group, phenethyloxycarbonylmethyl group, and 4-t-butylphenethyloxycarbonylmethyl group;

[0077]

a linear, branched, or cyclic 2-alkoxycarbonylethyl group such as a 2-methoxycarbonylethyl group, 2-ethoxycarbonylethyl group, 2-n-propoxycarbonylethyl group, 2-i-propoxycarbonylethyl group, 2-n-butoxycarbonylethyl group, 2-(2'-methylpropoxy)carbonylethyl group, 2-(1'-methylpropoxy)carbonylethyl group, 2-t-butoxycarbonylethyl group, 2-cyclohexyloxycarbonylethyl group, and 2-(4'-t-butylcyclohexyloxycarbonyl)ethyl group; a 2-aryloxycarbonylethyl group such as a 2-phenoxycarbonylethyl group, 2-(4'-t-butylphenoxycarbonyl)ethyl group, and 2-(1'-naphthyloxycarbonyl)ethyl group;

a 2-aralkyloxycarbonylethyl group such as a  
2-benzyloxycarbonylethyl group,  
2-(4'-t-butylbenzyloxycarbonyl)ethyl group,  
2-phenethyloxycarbonylethyl group, and 2-  
(4'-t-butylphenethyloxycarbonyl)ethyl group;  
a tetrahydrofuranyloxycarbonyl group,  
tetrahydropyranyloxycarbonyl group, and the like.

[0078]

Of these acid-dissociable groups (iii), in addition to  
t-butoxycarbonyl group and the groups shown by the formulas  
(ii-1), (ii-2), (ii-10), (ii-11), (ii-13), (ii-14), (ii-16),  
(ii-17), (ii-22), (ii-23), (ii-34), (ii-35), (ii-40), (ii-41),  
(ii-52), and (ii-53), groups corresponding to the formula  
-COOR' (wherein R' represents a linear, branched, or cyclic  
alkyl group having 1-19 carbon atoms) or the formula  
-COOCH<sub>2</sub>COOR'' (wherein R'' represents a linear, branched, or  
cyclic alkyl group having 1-17 carbon atoms) are preferable.

[0079]

As examples of linear or branched alkyl groups having 1-4  
carbon atoms represented by X or Y, a methyl group, ethyl group,  
n-propyl group, i-propyl group, n-butyl group, i-butyl group,  
sec-butyl group, t-butyl group, and the like can be given.

Of these alkyl groups, a methyl group, ethyl group, and  
the like are particularly preferable.

i in the formula (5) is preferably either 0 or 1.

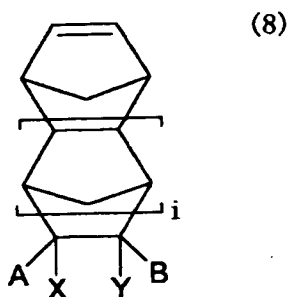
[0080]

As examples of monomers providing the recurring unit (7),

compounds shown by the following formula (8) (hereinafter referred to as "norbornene derivatives ( $\beta$ -1)") can be given.

[0081]

[Chemical Formula 36]



wherein A, B, X, Y, and i have the same meanings as defined for the formula (7).

[0082]

Given as examples of the norbornene derivatives ( $\beta$ -1) are a compound of the formula (8), wherein either one of A and B, or both, are the acid-dissociating groups (ii), the remainder of the A and B, X, and Y are hydrogen atoms, and i is 0;

a compound of the formula (8), wherein either one of A and B, or both, are the acid-dissociating groups (ii), the remainder of the A and B, X, and Y are hydrogen atoms, and i is 1;

5-methoxycarbonylbicyclo[2.2.1]hept-2-ene,

5-ethoxycarbonylbicyclo[2.2.1]hept-2-ene,

5-n-propoxycarbonylbicyclo[2.2.1]hept-2-ene,

5-i-propoxycarbonylbicyclo[2.2.1]hept-2-ene,

5-n-butoxycarbonylbicyclo[2.2.1]hept-2-ene,

5-(2'-methylpropoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5-(1'-methylpropoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5-t-butoxycarbonylbicyclo[2.2.1]hept-2-ene,  
 5-cyclopentyloxycarbonylbicyclo[2.2.1]hept-2-ene,  
 5-(1'-methylcyclopentyloxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5-cyclohexyloxycarbonylbicyclo[2.2.1]hept-2-ene,  
 5-(1'-methylcyclohexyloxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5-(4'-t-butylcyclohexyloxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5-phenoxy carbonylbicyclo[2.2.1]hept-2-ene,  
 5-(1'-ethoxyethoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5-(1'-cyclohexyloxyethoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5-t-butoxycarbonylmethoxycarbonylbicyclo[2.2.1]hept-2-ene,  
 5-tetrahydrofuranyloxycarbonylbicyclo[2.2.1]hept-2-ene,  
 5-tetrahydropyranyloxycarbonylbicyclo[2.2.1]hept-2-ene,  
 [0083]  
 5-methyl-5-methoxycarbonylbicyclo[2.2.1]hept-2-ene,  
 5-methyl-5-ethoxycarbonylbicyclo[2.2.1]hept-2-ene,  
 5-methyl-5-n-propoxycarbonylbicyclo[2.2.1]hept-2-ene,  
 5-methyl-5-i-propoxycarbonylbicyclo[2.2.1]hept-2-ene,  
 5-methyl-5-n-butoxycarbonylbicyclo[2.2.1]hept-2-ene,  
 5-methyl-5-(2'-methylpropoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5-methyl-5-(2'-methylpropoxycarbonyl)bicyclo[2.2.1]hept-2-



ene,  
 5-methyl-5-t-butoxycarbonylbicyclo[2.2.1]hept-2-ene,  
 5-methyl-5-cyclohexyloxycarbonylbicyclo[2.2.1]hept-2-ene,  
 5-methyl-5-(4'-t-butylcyclohexyloxycarbonyl)bicyclo[2.2.1]  
 hept-2-ene,  
 5-methyl-5-phenoxybicyclo[2.2.1]hept-2-ene,  
 5-methyl-5-(1'-ethoxyethoxycarbonyl)bicyclo[2.2.1]hept-2-  
 ene,  
 5-methyl-5-(1'-cyclohexyloxyethoxycarbonyl)bicyclo[2.2.1]  
 hept-2-ene,  
 5-methyl-5-t-butoxycarbonylmethoxycarbonylbicyclo[2.2.1]  
 hept-2-ene,  
 5-methyl-5-tetrahydrofuranyloxycarbonylbicyclo[2.2.1]hept-  
 2-ene,  
 5-methyl-5-tetrahydropyranyloxycarbonylbicyclo[2.2.1]hept-  
 2-ene,

[0084]

5,6-di(methoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5,6-di(ethoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5,6-di(n-propoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5,6-di(i-propoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5,6-di(n-butoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5,6-di(2'-methylpropoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5,6-di(1'-methylpropoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5,6-di(t-butoxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5,6-di(cyclopentyloxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5,6-di(1'-methylcyclopentyloxycarbonyl)bicyclo[2.2.1]hept-

2-ene,  
 5,6-di(cyclohexyloxycarbonyl)bicyclo[2.2.1]hept-2-ene,  
 5,6-di(1'-methylcyclohexyloxycarbonyl)bicyclo[2.2.1]hept-  
 2-ene,  
 5,6-di(4'-t-butylcyclohexyloxycarbonyl)bicyclo[2.2.1]hept-  
 2-ene,  
 5,6-di(phenoxy carbonyl)bicyclo[2.2.1]hept-2-ene,  
 5,6-di(1'-ethoxyethoxy carbonyl)bicyclo[2.2.1]hept-2-ene,  
 5,6-di(1'-cyclohexyloxyethoxy carbonyl)bicyclo[2.2.1]hept-  
 2-ene,  
 5,6-di(t-butoxycarbonylmethoxycarbonyl)bicyclo[2.2.1]hept- ✓  
 2-ene,  
 5,6-di(tetrahydrofuranyloxycarbonyl)bicyclo[2.2.1]hept-2-  
 ene,  
 5,6-di(tetrahydropyranyloxycarbonyl)bicyclo[2.2.1]hept-2-  
 ene,

[0085]

8-methoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-ethoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-n-propoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-i-propoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-n-butoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-(2'-methylpropoxy) carbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]  
 dodec-3-ene,  
 8-(1'-methylpropoxy) carbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]  
 dodec-3-ene,  
 8-t-butoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

8-cyclopentyloxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-(1'-methylcyclopentyloxycarbonyl)tetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-cyclohexyloxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-(1'-methylcyclohexyloxycarbonyl)tetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-(4'-t-butylcyclohexyloxy)carbonyltetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-phenoxy carbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-(1'-ethoxyethoxy)carbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]  
 dodec-3-ene,  
 8-(1'-cyclohexyloxyethoxy)carbonyltetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-t-butoxycarbonylmethoxycarbonyltetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-tetrahydrofuranyloxycarbonyltetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-tetrahydropyranyloxycarbonyltetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 [0086]  
 8-methyl-8-methoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-methyl-8-ethoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-methyl-8-n-propoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]

dodec-3-ene,  
 8-methyl-8-i-propoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]  
 dodec-3-ene,  
 8-methyl-8-n-butoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]  
 dodec-3-ene,  
 8-methyl-8-(2'-methylpropoxy) carbonyltetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodec-3-ene,  
 8-methyl-8-(1'-methylpropoxy) carbonyltetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodec-3-ene,  
 8-methyl-8-t-butoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] ✓  
 dodec-3-ene,  
 8-methyl-8-cyclohexyloxy carbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]  
 dodec-3-ene,  
 8-methyl-8-(4'-t-butylcyclohexyloxy) carbonyltetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodec-3-ene,  
 8-methyl-8-phenoxy carbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodec-  
 3-ene,  
 8-methyl-8-(1'-ethoxyethoxy) carbonyltetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodec-3-ene,  
 8-methyl-8-(1'-cyclohexyloxyethoxy) carbonyltetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodec-3-ene,  
 8-methyl-8-t-butoxycarbonylmethoxycarbonyltetracyclo ✓  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodec-3-ene,  
 8-methyl-8-tetrahydrofuranyloxy carbonyltetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodec-3-ene,  
 8-methyl-8-tetrahydropyranyloxy carbonyltetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>] dodec-3-ene,

[0087]

8,9-di(methoxycarbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8,9-di(ethoxycarbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8,9-di(n-propoxycarbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8,9-di(i-propoxycarbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8,9-di(n-butoxycarbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8,9-di(2'-methypropoxycarbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8,9-di(1'-methypropoxycarbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8,9-di(t-butoxycarbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8,9-di(cyclopentyloxy carbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8,9-di(1'-methylcyclopentyloxy carbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8,9-di(cyclohexyloxy carbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8,9-di(1'-methylcyclohexyloxy carbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
8,9-di(4'-t-butylcyclohexyloxy carbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

8,9-di(phenoxy-carbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,9-di(1'-ethoxyethoxy-carbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,9-di(1'-cyclohexyloxyethoxy-carbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,9-di(t-butoxy-carbonyl-methoxy-carbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,9-di(tetrahydrofuranyloxy-carbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,9-di(tetrahydropyranyloxy-carbonyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, and the like can be given.

[0088]

Of these norbornene derivatives ( $\beta$ -1), preferable compounds are a compound of the formula (8) in which either one of A and B or both are a t-butoxy-carbonyl group, 1-methylcyclopentyloxy-carbonyl group, 1-methylcyclohexyloxy-carbonyl group, or the groups shown by the formulas (ii-1), (ii-2), (ii-10), (ii-11), (ii-13), (ii-14), (ii-16), (ii-17), (ii-22), (ii-23), (ii-34), (ii-35), (ii-40), (ii-41), (ii-52), and (ii-53), the remainder of the A and B, X, and Y are a hydrogen atom, and i is 0; a compound of the formula (8) in which either one of A and B or both are a t-butoxy-carbonyl group, 1-methylcyclopentyloxy-carbonyl group, 1-methylcyclohexyloxy-carbonyl group, or the groups shown by the formulas (ii-1), (ii-2), (ii-10), (ii-11), (ii-13), (ii-14), (ii-16), (ii-17), (ii-22), (ii-23), (ii-34), (ii-35), (ii-40),

(ii-41), (ii-52), and (ii-53), the remainder of the A and B, X, and Y are a hydrogen atom, and i is 1;

5,6-di(t-butoxycarbonylmethoxycarbonyl)bicyclo[2.2.1]hept-2-ene, 8-methyl-8-t-butoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

8-methyl-8-t-butoxycarbonylmethoxycarbonyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, and the like.

These preferable norbornene derivatives ( $\beta$ -1) may also be used as a monomer which provides the other recurring unit (b) in the resin (A2) described later.

[0089]

The following compounds can be given as examples of monomers which provide the other recurring unit (a) other than the recurring unit (7): norbornenes such as norbornene (i.e. bicyclo[2.2.1]hept-2-ene), 5-methylbicyclo[2.2.1]hept-2-ene, 5-ethylbicyclo[2.2.1]hept-2-ene, 5-hydroxybicyclo[2.2.1]hept-2-ene, 5-hydroxymethylbicyclo[2.2.1]hept-2-ene, tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 8-methyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 8-ethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 8-hydroxytetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 8-hydroxymethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 8-fluorotetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 8-fluoromethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 8-difluoromethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

8-trifluoromethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-pentafluoroethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,8-difluorotetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,9-difluorotetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,8-bis(trifluoromethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,9-bis(trifluoromethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-methyl-8-trifluoromethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,8,9-trifluorotetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,8,9-tris(trifluoromethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

[0090]

8,8,9,9-tetrafluorotetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,8,9,9-tetrakis(trifluoromethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,8-difluoro-9,9-bis(trifluoromethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,9-difluoro-8,9-bis(trifluoromethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,8,9-trifluoro-9-trifluoromethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,8,9-trifluoro-9-trifluoromethoxytetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,8,9-trifluoro-9-pentafluoropropoxytetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,



8-fluoro-8-pentafluoroethyl-9,9-bis(trifluoromethyl)  
 tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,9-difluoro-8-heptafluoroisopropyl-9-  
 trifluoromethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-chloro-8,9,9-trifluorotetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-  
 ene,  
 8,9-dichloro-8,9-bis(trifluoromethyl)tetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-(2',2',2'-trifluorocarboethoxy)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]  
 dodec-3-ene,  
 8-methyl-8-(2',2',2'-trifluorocarboethoxy)tetracyclo  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, or derivatives of these  
 norbornenes (hereinafter collectively referred to as  
 "norbornene compounds (β-2);

[0091]

other alicyclic unsaturated compounds such as  
 dicyclopentadiene,  
 tricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene,  
 tricyclo[5.2.1.0<sup>2,6</sup>]dec-3-ene,  
 tricyclo[4.4.0.1<sup>2,5</sup>]undec-3-ene,  
 tricyclo[6.2.1.0<sup>1,8</sup>]undec-9-ene,  
 tricyclo[6.2.1.0<sup>1,8</sup>]undec-4-ene,  
 tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>.0<sup>1,6</sup>]dodec-3-ene,  
 8-methyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>.0<sup>1,6</sup>]dodec-3-ene,  
 8-ethylidenetetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,12</sup>]dodec-3-ene,  
 8-ethylidenetetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>.0<sup>1,6</sup>]dodec-3-ene,  
 pentacyclo[6.5.1.1<sup>3,6</sup>.0<sup>2,7</sup>.0<sup>9,13</sup>]pentadec-4-ene,

and pentacyclo[7.4.0.1<sup>2,5</sup>.1<sup>9,12</sup>.0<sup>8,13</sup>]pentadec-3-ene;

[0092]

(meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, n-butyl (meth)acrylate, 2-methylpropyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, cyclopropyl (meth)acrylate, cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate, cyclohexenyl (meth)acrylate, 4-methoxycyclohexyl (meth)acrylate, 2-cyclopropyloxycarbonylethyl (meth)acrylate, 2-cyclopentyloxycarbonylethyl (meth)acrylate, 2-cyclohexyloxycarbonylethyl (meth)acrylate, 2-cyclohexenyloxycarbonylethyl (meth)acrylate, 2-(4'-methoxycyclohexyl)oxycarbonylethyl (meth)acrylate, norbornyl (meth)acrylate, isobornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, tetracyclodecanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, adamantyl (meth)acrylate, adamantylmethyl (meth)acrylate, and 1-methyladamantyl (meth)acrylate;  $\alpha$ -hydroxymethylacrylates such as methyl  $\alpha$ -hydroxymethyl acrylate, ethyl  $\alpha$ -hydroxymethyl acrylate, n-propyl  $\alpha$ -hydroxymethyl acrylate, and n-butyl  $\alpha$ -hydroxymethyl acrylate;

[0093]

(meth)acryloyloxylactone compound having an acid-dissociable group such as

$\alpha$ -(meth)acryloyloxy- $\beta$ -methoxycarbonyl- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -ethoxycarbonyl- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -n-propoxycarbonyl- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -i-propoxycarbonyl- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -n-butoxycarbonyl- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -(2-methylpropoxy)carbonyl- $\gamma$ -  
butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -(1-methylpropoxy)carbonyl- $\gamma$ -  
butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -t-butoxycarbonyl- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -cyclohexyloxycarbonyl- $\gamma$ -  
butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -(4-t-butylcyclohexyloxy)carbonyl- $\gamma$ -  
butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -phenoxycarbonyl- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -(1-ethoxyethoxy)carbonyl- $\gamma$ -  
butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -(1-cyclohexyloxyethoxy)carbonyl- $\gamma$ -  
butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -t-butoxycarbonylmethoxycarbonyl- $\gamma$ -  
butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -tetrahydrofuranyloxycarbonyl- $\gamma$ -  
butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -tetrahydropyranyloxycarbonyl- $\gamma$ -  
butyrolactone,

[0094]

$\alpha$ -methoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -ethoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -n-propoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -i-propoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -n-butoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -(2-methylpropoxy)carbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -(1-methylpropoxy)carbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -t-butoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -cyclohexyloxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -(4-t-butylcyclohexyloxy)carbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -phenoxy carbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -(1-ethoxyethoxy)carbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -(1-cyclohexyloxyethoxy)carbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -t-butoxycarbonylmethoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -tetrahydrofuranyloxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
and  $\alpha$ -tetrahydropyranyloxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone;

[0095]

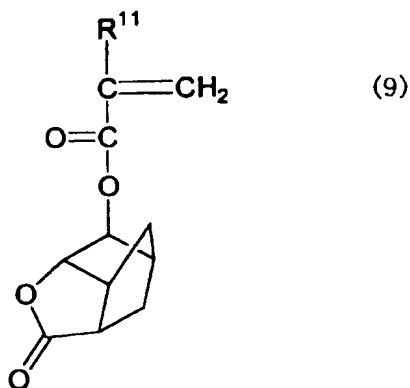
(meth)acryloyloxylactone compound having no acid-dissociable group such as

$\alpha$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -fluoro- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -hydroxy- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -methyl- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -ethyl- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ , $\beta$ -dimethyl- $\gamma$ -butyrolactone,  
 $\alpha$ -(meth)acryloyloxy- $\beta$ -methoxy- $\gamma$ -butyrolactone,  
 $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -fluoro- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -hydroxy- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -methyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -ethyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ , $\alpha$ -dimethyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  
 $\alpha$ -methoxy- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone, and  
 $\alpha$ -(meth)acryloyloxy- $\delta$ -mevalonolactone;

[0096]

compounds shown by the following formula (9),

[Chemical Formula 37]



wherein R<sup>11</sup> represents a hydrogen atom or a methyl group;

[0097]

vinyl esters such as vinyl acetate, vinyl propionate, and vinyl butyrate;

unsaturated nitrile compounds such as (meth)acrylonitrile,  $\alpha$ -chloroacrylonitrile, crotonitrile, maleinitrile, fumaronitrile, mesaconitrile, citraconitrile, and itaconitrile;

unsaturated amide compounds such as (meth)acrylamide, N,N-dimethyl(meth)acrylamide, crotonamide, maleinamide, fumaramide, mesaconamide, citraconamide, and itaconamide; other nitrogen-containing vinyl compounds such as N-vinyl- $\epsilon$ -caprolactam, N-vinylpyrrolidone, vinylpyridine, and vinylimidazole;

unsaturated carboxylic acids (anhydrides) such as (meth)acrylic acid, crotonic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, and mesaconic acid; carboxyl group-containing esters of unsaturated carboxylic acids such as 2-carboxyethyl (meth)acrylate, 2-carboxypropyl (meth)acrylate, 3-carboxypropyl (meth)acrylate, 4-carboxybutyl (meth)acrylate, 4-carboxycyclohexyl (meth)acrylate, carboxytricyclodecanyl (meth)acrylate, and carboxytetracyclodecanyl (meth)acrylate; and

mono-functional monomers, which include compounds in which a carboxyl group in the above unsaturated carboxylic acids or carboxyl group-containing esters of unsaturated carboxylic

acids is converted into the above acid-dissociable group (i);

[0098]

poly-functional monomers including  
methylene glycol di(meth)acrylate,  
ethylene glycol di(meth)acrylate,  
propylene glycol di(meth)acrylate,  
1,6-hexanediol di(meth)acrylate,  
2,5-dimethyl-2,5-hexanediol di(meth)acrylate,  
1,8-octanediol di(meth) acrylate,  
1,9-nonanediol di(meth) acrylate,  
1,4-bis(2-hydroxypropyl)benzene di(meth) acrylate,  
1,3-bis(2-hydroxypropyl)benzene di(meth) acrylate,  
1,2-adamantanediol di(meth) acrylate,  
1,3-adamantanediol di(meth) acrylate,  
1,4-adamantanediol di(meth) acrylate, and  
tricyclodecanyldimethylol di(meth) acrylate.

[0099]

The amount of the recurring unit (I) in the resin (A1) is 1-100 mol%, preferably 1-90 mol%, and still more preferably 5-80 mol% of the total amount of the recurring units. If the amount of the recurring unit (I) is less than 1 mol%, developability of the resulting radiation-sensitive resin composition tends to decrease.

[0100]

The amount of the recurring unit (I) in the resin (A1-1) is usually 1-50 mol%, preferably 1-40 mol%, and still more preferably 5-40 mol% of the total amount of the recurring units.

If the amount of the recurring unit (I) is less than 1 mol%, developability of the resulting radiation-sensitive resin composition tends to decrease. If the amount exceeds 50 mol%, on the other hand, resolution as a resist tends to decrease.

The amount of the recurring unit (II) is usually 1-50 mol%, preferably 5-50 mol%, and still more preferably 10-50 mol% of the total amount of the recurring units. If the content of the recurring unit (II) is less than 1 mol%, the rate of copolymerization decreases and the resulting radiation-sensitive resin composition tends to exhibit decreased developability. If the content exceeds 50 mol%, on the other hand, part of maleic anhydride, which is a monomer providing the recurring unit (II), may remain unreacted in the polymerization reaction for producing the resin (A1-1).

The amount of the other recurring units (a) is usually 40 mol% or less, and preferably 30 mol% or less.

[0101]

The amount of the recurring unit (I) in the resin (A1-2) is usually 1-50 mol%, preferably 5-50 mol%, and still more preferably 5-45 mol% of the total amount of the recurring units. If the amount of the recurring unit (I) is less than 1 mol%, developability of the resulting radiation-sensitive resin composition tends to decrease. If the amount exceeds 50 mol%, on the other hand, resolution as a resist tends to decrease.

The amount of the recurring unit (II) is usually 1-50 mol%, preferably 5-50 mol%, and still more preferably 5-45 mol% of the total amount of the recurring units. If the content of the



recurring unit (II) is less than 1 mol%, developability of the resulting radiation-sensitive resin composition tends to decrease. If the content exceeds 50 mol%, resolution as a resist tends to decrease.

The amount of the recurring unit (III) is usually 1-60 mol%, preferably 5-60 mol%, and still more preferably 10-60 mol% of the total amount of the recurring units. If the content of the recurring unit (III) is less than 1 mol%, resolution as a resist tends to decrease. If the content exceeds 60 mol%, undeveloped areas such as scum tends to be produced due to impaired developability of the resulting radiation-sensitive resin composition.

The amount of the other recurring units (a) is usually 40 mol% or less, and preferably 30 mol% or less.

[0102]

The resin (A1) can be prepared by polymerizing the norbornene derivatives ( $\alpha 1$ ), preferably together with maleic acid anhydride or maleic acid anhydride and a monomer which provides the recurring unit (III), and optionally with monomers which provide the other recurring units (a) in an appropriate solvent using a radical polymerization initiator such as hydroperoxides, dialkyl peroxides, diacyl peroxides, or azo compounds and, as required, in the presence of a chain-transfer agent.

As examples of the solvent used for polymerizing the components, alkanes such as n-pentane, n-hexane, n-heptane, n-octane, n-nonane, and n-decane; cycloalkanes such as

cyclohexane, cycloheptane, cyclooctane, decalin, and norbornane; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, and cumene; halogenated hydrocarbons such as chlorobutanes, bromohexanes, dichloroethanes, hexamethylene dibromide, and chlorobenzene; saturated carboxylic acid esters such as ethyl acetate, n-butyl acetate, i-butyl acetate, and methyl propionate; ethers such as tetrahydrofuran, dimethoxyethanes, and diethoxyethanes; and the like can be given.

These solvents may be used either individually or in combination of two or more.

The polymerization temperature is usually 40-120°C, and preferably 50-90°C. The reaction time is usually 1-48 hours, and preferably 1-24 hours.

[0103]

It is preferable that the resin (A1) of the present invention contains almost no impurities such as halogens or metals. The smaller the amount of such impurities, the better are the sensitivity, resolution, process stability, pattern shape, or the like as a resist. The resin (A1) can be purified using, for example, a chemical purification method such as washing with water or liquid-liquid extraction or a combination of the chemical purification method and a physical purification method such as ultrafiltration or centrifugation.

[0104]

Next, the resin (A2) will be explained.

As examples of the linear or branched alkyl group having

1-4 carbon atoms represented by  $R^8$ ,  $R^9$ , or  $R^{10}$  in the formula (5), a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, 2-methylpropyl group, 1-methylpropyl group, t-butyl group, and the like can be given.

As examples of the monovalent oxygen-containing polar group represented by  $R^8$ ,  $R^9$ , or  $R^{10}$ , a hydroxyl group; carboxyl group; linear or branched hydroxyalkyl groups having 1-4 carbon atoms such as a hydroxymethyl group, 1-hydroxyethyl group, 2-hydroxyethyl group, 1-hydroxy-n-propyl group, 2-hydroxy-n-propyl group, 3-hydroxy-n-propyl group, 1-hydroxy-n-butyl group, 2-hydroxy-n-butyl group, 3-hydroxy-n-butyl group, and 4-hydroxy-n-butyl group; linear or branched alkoxy groups having 1-4 carbon atoms such as a methoxy group, ethoxy group, n-propoxy group, i-propoxy group, n-butoxy group, 2-methylpropoxy group, 1-methylpropoxy group, and t-butoxy group; and the like can be given.

Of these oxygen-containing polar groups, a hydroxyl group, carboxyl group, hydroxymethyl group, methoxy group, ethoxy group, and the like are preferable.

[0105]

As examples of the monovalent nitrogen-containing polar group represented by  $R^8$ ,  $R^9$ , or  $R^{10}$ , a cyano group; linear or branched cyanoalkyl groups having 2-5 carbon atoms such as a cyanomethyl group, 1-cyanoethyl group, 2-cyanoethyl group, 1-cyano-n-propyl group, 2-cyano-n-propyl group, 3-cyano-n-propyl group, 1-cyano-n-butyl group, 2-cyano-n-butyl group, 3-cyano-n-butyl group, and

4-cyano-n-butyl group.

Of these nitrogen-containing polar groups, a cyano group, cyanomethyl group, 1-cyanoethyl group, and the like are preferable.

[0106]

Particularly preferable groups represented by  $R^8$ ,  $R^9$ , or  $R^{10}$  in the formula (5) are a hydrogen atom, methyl group, ethyl group, hydroxyl group, carboxyl group, hydroxymethyl group, methoxy group, ethoxy group, cyano group, cyanomethyl group, 1-cyanoethyl group, and the like.

m and n in the formula (5) are preferably either 0 or 1.

The structural unit (IV) may be used in the resin (A2) either individually or in combination of two or more.

[0107]

The structural unit (IV) can be formed in the resin (A2) by the ring-opening polymerization of a compound similar to the norbornene derivative ( $\alpha 1$ ) of the formula (6), but replacing  $R^3$ ,  $R^4$ , and  $R^5$  respectively with  $R^8$ ,  $R^9$ , and  $R^{10}$  (such a compound is hereinafter referred to as "norbornene derivative ( $\alpha 2$ )"), for example, in the presence of a metathesis catalyst described later.

The resin (A2) may further comprise one or more other structural units obtained by a ring opening polymerization using a metathesis catalyst (hereinafter referred to as "other structural unit (b)").

As examples of monomers which provide the other structural unit (b), the same norbornene derivatives ( $\beta-1$ ), norbornene

compounds ( $\beta$ -2), and other alicyclic unsaturated compounds given in connection with the resin (A1) can be given.

[0108]

The amount of the structural unit (IV) in the resin (A2) is usually 1-100 mol%, preferably 5-90 mol%, and still more preferably 10-80 mol% of the total amount of the structural units. If the amount of the structural unit (IV) is less than 1 mol%, developability of the resulting radiation-sensitive resin composition tends to decrease.

[0109]

The resin (A2) is prepared by the ring-opening (co)polymerization of a norbornene derivative ( $\alpha$ 2), optionally together with a norbornene derivative ( $\beta$ -1), norbornene compound ( $\beta$ -2), and other monomers such as an alicyclic unsaturated compound which is copolymerizable by the ring-opening (co)polymerization in an appropriate solvent using a metathesis catalyst.

[0110]

The metathesis catalyst is usually a combination of at least one compound of an element selected from the group consisting of W, Mo, and Re (hereinafter referred to as "specific transition metal compound") and at least one compound of a metal belonging to the group IA, IIA, IIIA, IVA, or IVB of Deming's Periodic Table and having a metal-carbon bond or metal-hydrogen bond (hereinafter referred to as "specific organometallic compound").

As examples of the specific transition metal compound, a

halide, oxyhalide, alkoxyhalide, alkoxide, carbonate, (oxy)acetylacetonate, carbonyl complex, acetonitrile complex, and hydride complex of W, Mo, or Re, and derivatives of these compounds can be given. Of these compounds, a compound of W or Mo, more particularly a halide, oxyhalide, or alkoxyhalide of W or Mo are preferable in view of polymerization activity and practicability.

The specific transition metal compound can be a compound conjugated by a suitable complexing agent such as triphenylphosphine ( $\text{P}(\text{C}_6\text{H}_5)_3$ ), pyridine ( $\text{NC}_5\text{H}_5$ ), or the like.

[0111]

The following compounds can be given as specific examples of the specific transition metal compound:  $\text{WCl}_6$ ,  $\text{WCl}_5$ ,  $\text{WCl}_4$ ,  $\text{WBr}_6$ ,  $\text{WF}_6$ ,  $\text{WI}_6$ ,  $\text{MoCl}_5$ ,  $\text{MoCl}_4$ ,  $\text{MoCl}_3$ ,  $\text{ReCl}_3$ ,  $\text{WOCl}_4$ ,  $\text{WOCl}_3$ ,  $\text{WOBr}_3$ ,  $\text{MoOCl}_3$ ,  $\text{MoOBr}_3$ ,  $\text{ReOCl}_3$ ,  $\text{ReOBr}_3$ ,  $\text{WCl}_2(\text{OC}_2\text{H}_5)_4$ ,  $\text{W}(\text{OC}_2\text{H}_5)_6$ ,  $\text{MoCl}_3(\text{OC}_2\text{H}_5)_2$ ,  $\text{Mo}(\text{OC}_2\text{H}_5)_5$ ,  $\text{WO}_2(\text{acac})_2$  (wherein "acac" indicates an acetylacetonate residue),  $\text{MoO}_2(\text{acac})_2$ ,  $\text{W}(\text{OCOR})_5$  (wherein "OCOR" indicates a carboxylic acid residue),  $\text{Mo}(\text{OCOR})_5$ ,  $\text{W}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ ,  $\text{Re}_2(\text{CO})_{10}$ ,  $\text{WCl}_5 \cdot \text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{MoCl}_5 \cdot \text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{ReOBr}_3 \cdot \text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{WCl}_6 \cdot \text{NC}_5\text{H}_5$ ,  $\text{W}(\text{CO})_5 \cdot \text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{W}(\text{CO})_3 \cdot (\text{CH}_3\text{CN})_3$ , and the like.

Of these,  $\text{WCl}_6$ ,  $\text{MoCl}_5$ ,  $\text{WCl}_2(\text{OC}_2\text{H}_5)_4$ ,  $\text{MoCl}_3(\text{OC}_2\text{H}_5)_2$ , and the like are preferable.

These specific transition metal compounds may be used either individually or in combinations of two or more.

The specific transition metal compound component which constitutes a metathesis catalyst may be a mixture of two or

more compounds forming specific transition metal compound by reacting in the polymerization reaction system.

[0112]

The following compounds can be given as specific examples of the specific organometallic compounds:  $n\text{-C}_4\text{H}_9\text{Li}$ ,  $n\text{-C}_5\text{H}_{11}\text{Na}$ ,  $\text{C}_6\text{H}_5\text{Na}$ ,  $\text{CH}_3\text{MgI}$ ,  $\text{C}_2\text{H}_5\text{MgBr}$ ,  $\text{CH}_3\text{MgBr}$ ,  $n\text{-C}_3\text{H}_7\text{MgCl}$ ,  $t\text{-C}_4\text{H}_9\text{MgCl}$ ,  $\text{CH}_2=\text{CHCH}_2\text{MgCl}$ ,  $(\text{C}_2\text{H}_5)_2\text{Zn}$ ,  $(\text{C}_2\text{H}_5)_2\text{Cd}$ ,  $\text{CaZn}(\text{C}_2\text{H}_5)_4$ ,  $(\text{CH}_3)_3\text{B}$ ,  $(\text{C}_2\text{H}_5)_3\text{B}$ ,  $(n\text{-C}_4\text{H}_9)_3\text{B}$ ,  $(\text{CH}_3)_3\text{Al}$ ,  $(\text{CH}_3)_2\text{AlCl}$ ,  $\text{CH}_3\text{AlCl}_2$ ,  $(\text{CH}_3)_3\text{Al}_2\text{Cl}_3$ ,  $(\text{C}_2\text{H}_5)_3\text{Al}$ ,  $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$ ,  $(\text{C}_2\text{H}_5)_2\text{Al} \cdot \text{O}(\text{C}_2\text{H}_5)_2$ ,  $(\text{C}_2\text{H}_5)_2\text{AlCl}$ ,  $\text{C}_2\text{H}_5\text{AlCl}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{AlH}$ ,  $(\text{C}_2\text{H}_5)_2\text{AlOC}_2\text{H}_5$ ,  $(\text{C}_2\text{H}_5)_2\text{AlCN}$ ,  $\text{LiAl}(\text{C}_2\text{H}_5)_2$ ,  $(n\text{-C}_3\text{H}_7)_3\text{Al}$ ,  $(i\text{-C}_4\text{H}_9)_3\text{Al}$ ,  $(i\text{-C}_4\text{H}_9)_2\text{AlH}$ ,  $(n\text{-C}_6\text{H}_{13})_3\text{Al}$ ,  $(n\text{-C}_8\text{H}_{17})_3\text{Al}$ ,  $(\text{C}_6\text{H}_5)_3\text{Al}$ ,  $(\text{CH}_3)_4\text{Ga}$ ,  $(\text{CH}_3)_4\text{Sn}$ ,  $(n\text{-C}_4\text{H}_9)_4\text{Sn}$ ,  $(\text{C}_2\text{H}_5)_3\text{SnH}$ ,  $\text{LiH}$ ,  $\text{NaH}$ ,  $\text{B}_2\text{H}_6$ ,  $\text{NaBH}_4$ ,  $\text{AlH}_3$ ,  $\text{LiAlH}_4$ ,  $\text{TiH}_4$ , and the like.

Of these,  $(\text{CH}_3)_3\text{Al}$ ,  $(\text{CH}_3)_2\text{AlCl}$ ,  $\text{CH}_3\text{AlCl}_2$ ,  $(\text{CH}_3)_3\text{Al}_2\text{Cl}_3$ ,  $(\text{C}_2\text{H}_5)_3\text{Al}$ ,  $(\text{C}_2\text{H}_5)_2\text{AlCl}$ ,  $\text{C}_2\text{H}_5\text{AlCl}_2$ ,  $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$ ,  $(\text{C}_2\text{H}_5)_2\text{AlH}$ ,  $(\text{C}_2\text{H}_5)_2\text{AlOC}_2\text{H}_5$ ,  $(\text{C}_2\text{H}_5)_2\text{AlCN}$ ,  $(n\text{-C}_3\text{H}_7)_3\text{Al}$ ,  $(i\text{-C}_4\text{H}_9)_3\text{Al}$ ,  $(i\text{-C}_4\text{H}_9)_2\text{AlH}$ ,  $(n\text{-C}_6\text{H}_{13})_3\text{Al}$ ,  $(n\text{-C}_8\text{H}_{17})_3\text{Al}$ ,  $(\text{C}_6\text{H}_5)_3\text{Al}$ , and the like are preferable.

These specific organometallic compounds may be used either individually or in combinations of two or more.

The atomic ratio of the specific transition metal compound and specific organometallic compound is from 1:1 to 1:100, preferably from 1:2 to 1:50.

[0113]

One or more activation agents (a) to (i) may be added to the catalyst consisting of a combination of the specific transition metal compound and specific organometallic compound

to promote the catalyst activity.

Activation Agent (a): Boron compounds such as B,  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  
 $\text{B}(\text{O}-n\text{-C}_4\text{H}_9)_3$ ,  $\text{BF}_3 \cdot \text{O}(\text{CH}_3)_2$ ,  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ ,  
 $\text{BF}_3 \cdot \text{O}(n\text{-C}_4\text{H}_9)_2$ ,  $\text{BF}_3 \cdot 2\text{C}_6\text{H}_5\text{OH}$ ,  $\text{BF}_3 \cdot 2\text{CH}_3\text{COOH}$ ,  
 $\text{BF}_3 \cdot \text{CO}(\text{NH}_2)_2$ ,  $\text{BF}_3 \cdot \text{N}(\text{C}_2\text{H}_4\text{OH})_3$ ,  $\text{BF}_3 \cdot$   
piperidine,  $\text{BF}_3 \cdot \text{NH}_2\text{C}_2\text{H}_5$ ,  $\text{B}_2\text{O}_3$ , and  $\text{H}_3\text{BO}_3$ ;  
silicon compounds such as  $\text{Si}(\text{OC}_2\text{H}_5)_4$  and  
 $\text{Si}(\text{Cl})_4$ .

Activation Agent (b): Alcohols, hydroperoxides,  
dialkylperoxides, and diacylperoxides.

Activation Agent (c): Water

Activation Agent (d): Oxygen

Activation Agent (e): Aldehydes, carbonyl compounds such as  
ketones, and oligomers or polymers of  
these compounds

Activation Agent (f): Cyclic ethers such as ethylene oxide,  
epichlorohydrin, and oxetane

Activation Agent (g): amides such as N,N-dimethylformamide  
and N,N-dimethylacetamide; amines such  
as aniline, morpholine, and piperidine;  
and azo compounds such as azobenzene

Activation Agent (h): N-nitroso compounds such as  
N-nitrosodimethylamine,  
N-nitrosodiphenylamine

Activation Agent (i): Compounds having a nitrogen-chlorine  
bond or a sulfur-chlorine bond such as  
trichloromelamine,



N-chlorosuccinimide, and  
phenylsulfenyl chloride

The ratio of these activators and specific transition metal compound cannot be generically specified because the ratio may considerably vary according to the type of the activator used. In many cases, the ratio is in the range from 0.005:1 to 10:1, and preferably from 0.05:1 to 3.0:1.

[0114]

Although the molecular weight of the resin (A2) obtained by the ring-opening (co)polymerization can be controlled by changing the reaction conditions such as the type and concentration of the metathesis catalyst, polymerization temperature, the type and amount of the solvent, the monomer concentration, and the like, the molecular weight control by adding a suitable molecular weight modifier to the reaction system is preferable.

As examples of the molecular weight modifier,  $\alpha$ -olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, and 1-decene;  $\alpha,\omega$ -diolefins such as 1,3-butadiene and 1,4-pentadiene; vinyl aromatic compounds such as styrene and  $\alpha$ -methylstyrene; acetylenes; and polar allyl compounds such as allyl chloride, allyl acetate, and trimethylallyloxysilane; and the like can be given.

These molecular weight modifiers may be used either individually or in combinations of two or more.

The amount of the molecular weight modifiers is usually 0.005-2 mol, preferably 0.02-1.0 mol, and still more preferably

0.02-0.7 mol for one mol of all the monomers.

As examples of the solvent used for the ring-opening (co)polymerization, alkanes such as n-pentane, n-hexane, n-heptane, n-octane, n-nonane, and n-decane; cycloalkanes such as cyclohexane, cycloheptane, cyclooctane, decalin, and norbornane; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, and cumene; halogenated hydrocarbons such as chlorobutane, bromohexane, dichloroethane, hexamethylene dibromide, and chlorobenzene; saturated carboxylic acid esters such as ethyl acetate, n-butyl acetate, i-butyl acetate, and methyl propionate; and the like can be given.

These solvents may be used either individually or in combination of two or more.

[0115]

From the viewpoint of transmittance of radioactive rays, the resin (A2) of the present invention preferably contains as small an amount of carbon-carbon unsaturated bonds as possible. Such a resin (A2) can be prepared by effecting an addition reaction such as a hydrogenation reaction, hydration reaction, halogenation reaction, and halogenation-hydrogenation reaction at an appropriate time during the course of the ring-opening (co)polymerization or after the ring-opening (co)polymerization. A particularly preferable resin (A2) is that obtained by the hydrogenation reaction.

The degree of hydrogenation of the hydrogenated resin (A2) is preferably 70% or more, more preferably 90% or more, and still

more preferably 100%.

A catalyst commonly used in the hydrogenation reaction of olefin compounds can be used in the above hydrogenation reaction.

As examples of a heterogeneous catalyst among such hydrogenation catalysts, a solid catalyst with a noble metal, such as Pd, Pt, Ni, Rh, or Ru, carried on a carrier such as carbon, silica, alumina, or titanium dioxide can be given. These heterogeneous catalysts may be used either individually or in combinations of two or more.

As examples of a homogeneous catalyst, a nickel naphthenate/triethylaluminum catalyst, nickel acetylacetonate/triethylaluminum catalyst, cobalt octenate/n-butyl lithium catalyst, titanocene dichloride/diethylaluminum monochloride catalyst, and a rhodium catalyst such as rhodium acetate, chlorotris(triphenylphosphine) rhodium, and the like can be given. These homogeneous catalysts may be used either individually or in combinations of two or more.

Of these hydrogenation catalysts, the heterogeneous system catalysts are preferable due to the high reaction activity, ease of catalyst removal after the reaction, and excellent color tone of the resulting resin (A2).

The hydrogenation reaction is carried out under a hydrogen gas pressure from atmospheric pressure to 300 atm, and preferably from 3 to 200 atm, at a temperature of usually 0-200°C, and preferably 20-180°C.

[0116]

Furthermore, the resin (A2) of the present invention should contain as small an amount of impurities as possible. The impurities mainly originate from the catalyst used in the ring-opening (co)polymerization reaction. Impurities to which particular attention should be paid when the resin composition is used as a resist are halogens such as fluorine, chlorine, and bromine, and metals belonging to the group IV, V, VI, VII, or VIII of the Deming's Periodic Table.

A preferable resin (A2) should contain halogen impurities of no more than 3 ppm, particularly no more than 2 ppm, and metal impurities no more than 300 ppb, and particularly no more than 100 ppb. The impurity content less than the above-described limit ensures sensitivity, resolution, and process stability as a resist and increases the yield of semiconductors produced using the radiation-sensitive resin composition of the present invention.

As the method for reducing impurities in the resin (A2) when the impurities are remaining halogens, (1) a method of washing or extracting (liquid-liquid extraction) the resin solution with purified water, (2) a combination of washing or liquid-liquid extraction with purified water and a physical purification method such as ultrafiltration, centrifugation, and the like, (3) a method of using an alkaline aqueous solution or an acid aqueous solution instead of purified water in the methods (1) or (2), and the like can be given. When the impurities are residual metals, in addition to the methods

(1)-(3), (4) a method of treating the resin by oxidation, reduction, ligand exchange, counter-ion exchange, etc. to increase the solubility of the residual metals in solvents or water, then applying the method (1), (2), or (3) can be given.

These treatments for reducing the amount of impurities can be carried out at an appropriate time after the ring-opening (co)polymerization for manufacturing the resin (A2).

[0117]

The resin (A) of the present invention has an acid-dissociating group. Therefore, when the group  $R^1$  in the structure (1) of the resin (A) is a group other than the acid-dissociating group (i), a monomer having an acid-dissociating group must be copolymerized with the norbornene derivatives ( $\alpha 1$ ) or norbornene derivatives ( $\alpha 2$ ), for example. Such a monomer having an acid-dissociating group may also be used when the group  $R^1$  is an acid-dissociating group (i).

[0118]

The polystyrene-reduced weight average molecular weight (hereinafter referred to as "Mw") of the resin (A) determined by gel permeation chromatography (GPC) is usually 3,000-300,000, preferably 4,000-200,000, and still more preferably 5,000-100,000. If Mw of the resin (A) is less than 3,000, heat resistance as a resist tends to decrease. If Mw exceeds 300,000, developability as a resist tends to decrease.

The ratio of Mw to the polystyrene-reduced number average molecular weight (hereinafter referred to as "Mn") determined

by gel permeation chromatography (GPC) ( $M_w/M_n$ ) of the resin (A) is usually 1-5, and preferably 1-3.

In the present invention, the resin (A) may be used either individually or in combination of two or more.

[0119]

#### Component (B)

The component (B) of the present invention is a photoacid generator which generates an acid upon exposure (hereinafter referred to as "acid generator (B)").

The acid generator (B) causes the acid-dissociable group in the resin (A) to dissociate by the action of an acid generated upon exposure. As a result, exposed areas of the resist film become readily soluble in an alkaline developer, whereby a positive-tone resist pattern is formed.

As examples of the acid generator (B), onium salt compounds, halogen-containing compounds, diazoketone compounds, sulfone compounds, sulfonate compounds, and the like can be given.

Examples of the acid generator (B) are given below.

[0120]

#### Onium salt compounds:

As examples of onium salt compounds, iodonium salts, sulfonium salts (including tetrahydrothiophenium salts), phosphonium salts, diazonium salts, pyridinium salts, and the like can be given.

Specific examples of preferable onium salt compounds include:

diphenyliodonium trifluoromethanesulfonate,

diphenyliodonium nonafluoro-n-butanesulfonate,  
 diphenyliodonium perfluoro-n-octanesulfonate,  
 bis(4-t-butylphenyl)iodoniumtrifluoromethane sulfonate,  
 bis(4-t-butylphenyl)iodonium nonafluoro-n-butanesulfonate,  
 bis(4-t-butylphenyl)iodonium perfluoro-n-octanesulfonate,  
 triphenylsulfonium trifluoromethanesulfonate,  
 triphenylsulfonium nonafluoro-n-butanesulfonate,  
 triphenylsulfonium perfluoro-n-octanesulfonate,  
 triphenylsulfonium 10-camphorsulfonate,  
 cyclohexyl·2-oxocyclohexyl·methylsulfoniumtrifluoromethane  
 sulfonate,  
 dicyclohexyl·2-oxocyclohexylsulfoniumtrifluoromethane  
 sulfonate,  
 2-oxocyclohexyldimethylsulfoniumtrifluoromethanesulfonate,  
 1-naphthyldimethylsulfonium trifluoromethanesulfonate,  
 1-naphthyldiethylsulfonium trifluoromethanesulfonate,  
 4-cyano-1-naphthyldimethylsulfonium  
 trifluoromethanesulfonate,  
 4-nitro-1-naphthyldimethylsulfonium  
 trifluoromethanesulfonate,  
 4-methyl-1-naphthyldimethylsulfonium  
 trifluoromethanesulfonate,  
 4-cyano-1-naphthyldiethylsulfonium  
 trifluoromethanesulfonate,  
 4-nitro-1-naphthyldiethylsulfonium  
 trifluoromethanesulfonate,  
 4-methyl-1-naphthyldiethylsulfonium

trifluoromethanesulfonate,  
 4-hydroxy-1-naphthyl dimethylsulfonium  
 trifluoromethanesulfonate,  
 [0121]  
 4-hydroxy-1-naphthyl tetrahydrothiophenium  
 trifluoromethanesulfonate,  
 4-hydroxy-1-naphthyl tetrahydrothiophenium  
 nonafluoro-n-butanesulfonate,  
 4-hydroxy-1-naphthyl tetrahydrothiophenium  
 perfluoro-n-octanesulfonate,  
 4-methoxy-1-naphthyl tetrahydrothiophenium  
 trifluoromethanesulfonate,  
 4-methoxy-1-naphthyl tetrahydrothiophenium  
 nonafluoro-n-butanesulfonate,  
 4-methoxy-1-naphthyl tetrahydrothiophenium  
 perfluoro-n-octanesulfonate,  
 4-ethoxy-1-naphthyl tetrahydrothiophenium  
 trifluoromethanesulfonate,  
 4-ethoxy-1-naphthyl tetrahydrothiophenium  
 nonafluoro-n-butanesulfonate,  
 4-ethoxy-1-naphthyl tetrahydrothiophenium  
 perfluoro-n-octanesulfonate,  
 4-n-butoxy-1-naphthyl tetrahydrothiophenium  
 trifluoromethanesulfonate,  
 4-n-butoxy-1-naphthyl tetrahydrothiophenium  
 nonafluoro-n-butanesulfonate,  
 4-n-butoxy-1-naphthyl tetrahydrothiophenium



perfluoro-n-octanesulfonate,  
4-methoxymethoxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,  
4-methoxymethoxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
4-methoxymethoxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,  
4-ethoxymethoxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,  
4-ethoxymethoxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
4-ethoxymethoxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,

[0122]

4-(1'-methoxyethoxy)-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,  
4-(1'-methoxyethoxy)-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
4-(1'-methoxyethoxy)-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,  
4-(2'-methoxyethoxy)-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,  
4-(2'-methoxyethoxy)-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
4-(2'-methoxyethoxy)-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,  
4-methoxycarbonyloxy-1-naphthyltetrahydrothiophenium

trifluoromethanesulfonate,  
4-methoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
4-methoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,  
4-ethoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,  
4-ethoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
4-ethoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,  
4-n-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,  
4-n-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
4-n-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,  
4-i-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,  
4-i-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
4-i-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,

[0123]

4-n-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,  
4-n-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium

nonafluoro-n-butanesulfonate,  
 4-n-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
 perfluoro-n-octanesulfonate,  
 4-t-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
 trifluoromethanesulfonate,  
 4-t-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
 nonafluoro-n-butanesulfonate,  
 4-t-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
 perfluoro-n-octanesulfonate,  
 4-(2'-tetrahydrofuryloxy)-1-naphthyltetrahydrothiophenium  
 trifluoromethanesulfonate,  
 4-(2'-tetrahydroxyfuryloxy)-1-naphthyltetrahydrothiophenium  
 nonafluoro-n-butanesulfonate,  
 4-(2'-tetrahydrofuryloxy)-1-naphthyltetrahydrothiophenium  
 perfluoro-n-octanesulfonate,  
 4-(2'-tetrahydropyryloxy)-1-naphthyltetrahydrothiophenium  
 trifluoromethanesulfonate,  
 4-(2'-tetrahydropyryloxy)-1-naphthyltetrahydrothiophenium  
 nonafluoro-n-butanesulfonate,  
 4-(2'-tetrahydropyryloxy)-1-naphthyltetrahydrothiophenium  
 perfluoro-n-octanesulfonate,  
 4-benzyloxy-1-naphthyltetrahydrothiopheniumtrifluoromethane  
 sulfonate,  
 4-benzyloxy-1-naphthyltetrahydrothiophenium  
 nonafluoro-n-butanesulfonate,  
 4-benzyloxy-1-naphthyltetrahydrothiophenium  
 perfluoro-n-octanesulfonate,

1-(1'-naphthylacetomethyl)tetrahydrothiophenium  
trifluoromethanesulfonate,  
1-(1'-naphthylacetomethyl)tetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
1-(1'-naphthylacetomethyl)tetrahydrothiophenium  
perfluoro-n-octanesulfonate,  
1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium  
trifluoromethanesulfonate,  
1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium  
perfluoro-n-octanesulfonate,  
and the like can be given.

[0124]

Halogen-containing compounds:

As examples of halogen-containing compounds, haloalkyl  
group-containing hydrocarbon compounds, haloalkyl  
group-containing heterocyclic compounds, and the like can be  
given.

As specific examples of preferable halogen-containing  
compounds, (trichloromethyl)-s-triazine derivatives such as  
phenylbis(trichloromethyl)-s-triazine,  
4-methoxyphenylbis(trichloromethyl)-s-triazine, and  
1-naphthylbis(trichloromethyl)-s-triazine,  
1,1-bis(4'-chlorophenyl)-2,2,2-trichloroethane, and the like  
can be given.

Diazoketone compounds:

As examples of diazoketone compounds, 1,3-diketo-2-diazo compounds, diazobenzoquinone compounds, diazonaphthoquinone compounds, and the like can be given.

As specific examples of preferable diazoketone compounds, 1,2-naphthoquinonediazido-4-sulfonyl chloride, 1,2-naphthoquinonediazido-5-sulfonyl chloride, 1,2-naphthoquinonediazido-4-sulfonate or 1,2-naphthoquinonediazido-5-sulfonate of 2,3,4,4'-tetrahydroxybenzophenone, 1,2-naphthoquinonediazido-4-sulfonate or 1,2-naphthoquinonediazido-5-sulfonate of 1,1,1-tris(4'-hydroxyphenyl)ethane, and the like can be given.

[0125]

#### Sulfone compounds:

As examples of the sulfone compounds,  $\beta$ -ketosulfone,  $\beta$ -sulfonylsulfone,  $\alpha$ -diazo compounds of these compounds, and the like can be given.

As specific examples of preferable sulfone compounds, 4-trisphenacylsulfone, mesitylphenacylsulfone, bis(phenylsulfonyl)methane, and the like can be given.

#### Sulfonate compounds:

As examples of the sulfonate compounds, alkyl sulfonate, alkylimide sulfonate, haloalkyl sulfonate, aryl sulfonate, imino sulfonate, and the like can be given.

As specific examples of preferable sulfonate compounds, benzointosylate, tris(trifluoromethanesulfonate) of pyrogallol, nitrobenzyl-9,10-diethoxyanthracene-2-sulfonate,

trifluoromethanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-  
 dicarbodiimide,  
 nonafluoro-n-butanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-  
 dicarbodiimide,  
 perfluoro-n-octanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-  
 dicarbodiimide,  
 N-hydroxysuccinimide-trifluoromethanesulfonate,  
 N-hydroxysuccinimide-nonafluoro-n-butanesulfonate,  
 N-hydroxysuccinimide-perfluoro-n-octanesulfonate,  
 1,8-naphthalenedicarboxylic acid imide  
 trifluoromethanesulfonate, and the like can be given.

[0126]

Of these acid generators (B), the following compounds are particularly preferable:

diphenyliodonium trifluoromethanesulfonate,  
 diphenyliodonium nonafluoro-n-butanesulfonate,  
 diphenyliodonium perfluoro-n-octanesulfonate,  
 bis(4-t-butylphenyl)iodoniumtrifluoromethane sulfonate,  
 bis(4-t-butylphenyl)iodonium nonafluoro-n-butanesulfonate,  
 bis(4-t-butylphenyl)iodonium perfluoro-n-octanesulfonate,  
 triphenylsulfonium trifluoromethanesulfonate,  
 triphenylsulfonium nonafluoro-n-butanesulfonate,  
 triphenylsulfonium perfluoro-n-octanesulfonate,  
 cyclohexyl·2-oxocyclohexyl·methylsulfoniumtrifluoromethane  
 sulfonate,  
 dicyclohexyl·2-oxocyclohexylsulfoniumtrifluoromethane  
 sulfonate,

2-oxocyclohexyldimethylsulfoniumtrifluoromethanesulfonate,  
4-hydroxy-1-naphthyldimethylsulfonium  
trifluoromethanesulfonate,

[0127]

4-hydroxy-1-naphthyltetrahydrothiopheniumtrifluoromethane  
sulfonate,

4-hydroxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,

4-hydroxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,

1-(1'-naphthylacetomethyl)tetrahydrothiophenium  
trifluoromethanesulfonate,

1-(1'-naphthylacetomethyl)tetrahydrothiophenium  
nonafluoro-n-butanesulfonate,

1-(1'-naphthylacetomethyl)tetrahydrothiophenium  
perfluoro-n-octanesulfonate,

1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium  
trifluoromethanesulfonate,

1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium  
nonafluoro-n-butanesulfonate,

1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium  
perfluoro-n-octanesulfonate,

[0128]

trifluoromethanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-  
dicarbodiimide,

nonafluoro-n-butanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-  
dicarbodiimide,

perfluoro-n-octanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-dicarbodiimide,  
N-hydroxysuccimide trifluoromethanesulfonate,  
N-hydroxysuccimide nonafluoro-n-butanesulfonate,  
N-hydroxysuccimide perfluoro-n-octanesulfonate,  
1,8-naphthalenedicarboxylic acid imide  
trifluoromethanesulfonate,  
and the like.

[0129]

In the present invention, the acid generator (B) may be used either individually or in combination of two or more.

The amount of the acid generator (B) to be used in the present invention is usually 0.1-10 parts by weight, and preferably 0.5-7 parts by weight for 100 parts by weight of the resin (A) from the viewpoint of ensuring sensitivity and developability as a resist. If the amount of the acid generator (B) is less than 0.1 part by weight, sensitivity and developability may decrease. If the amount exceeds 10 parts by weight, a rectangular resist pattern may not be obtained due to decreased radiation transmittance.

[0130]

#### Additives

It is preferable to add an acid diffusion controller to the radiation-sensitive resin composition of the present invention. The acid diffusion controller controls diffusion of an acid generated from the acid generator (B) upon exposure in the resist film to hinder unfavorable chemical reactions in



the unexposed area.

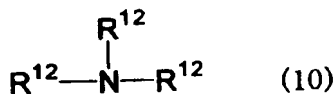
The addition of such an acid diffusion controller improves storage stability of the resulting radiation-sensitive resin composition and resolution as a resist. Moreover, the addition of the acid diffusion controller prevents the line width of the resist pattern from changing due to changes in the post-exposure delay (PED) between exposure and development, whereby a composition with remarkably superior process stability can be obtained.

As the acid diffusion controller, organic compounds containing nitrogen of which the basicity does not change during exposure or heating for forming a resist pattern are preferable.

As the organic compounds containing nitrogen, for example, the compounds shown in the following formula (10),

[0131]

[Chemical Formula 38]



(wherein  $\text{R}^{12}$  individually represents a hydrogen atom, a substituted or unsubstituted, linear, branched, or cyclic alkyl group, substituted or unsubstituted aryl group, or substituted or unsubstituted aralkyl group)

[0132]

(hereinafter called "nitrogen-containing compounds (a)"),

compounds having two nitrogen atoms in the molecule (hereinafter called "nitrogen-containing compounds (b)"), polyamino compounds or polymers having three or more nitrogen atoms (hereinafter collectively called "nitrogen-containing compounds (c)"), quaternary ammonium hydroxide compounds, amide group-containing compounds, urea compounds, nitrogen-containing heterocyclic compounds, and the like can be given.

[0133]

Examples of the nitrogen-containing compounds (a) include mono(cyclo)alkylamines such as n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, n-decylamine, and cyclohexylamine; di(cyclo)alkylamines such as di-n-butylamine, di-n-pentylamine, di-n-hexylamine, di-n-heptylamine, di-n-octylamine, di-n-nonylamine, di-n-decylamine, cyclohexylmethanamine, and dicyclohexylamine; tri(cyclo)alkylamines such as triethylamine, tri-n-propylamine, tri-n-butylamine, tri-n-pentylamine, tri-n-hexylamine, tri-n-heptylamine, tri-n-octylamine, tri-n-nonylamine, tri-n-decylamine, cyclohexyldimethanamine, dicyclohexylmethanamine, and tricyclohexylamine; aromatic amines such as aniline, N-methylaniline, N,N-dimethylaniline, 2-methylaniline, 3-methylaniline, 4-methylaniline, 4-nitroaniline, diphenylamine, triphenylamine, and naphthylamine; and the like.

[0134]

Examples of the nitrogen-containing compound (b) include

ethylenediamine, N,N,N',N'-tetramethylethylenediamine,  
tetramethylenediamine, hexamethylenediamine,  
4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether,  
4,4'-diaminobenzophenone, 4,4'-diaminodiphenylamine,  
2,2-bis(4'-aminophenyl)propane,  
2-(3'-aminophenyl)-2-(4'-aminophenyl)propane,  
2-(4'-aminophenyl)-2-(3'-hydroxyphenyl)propane,  
2-(4'-aminophenyl)-2-(4'-hydroxyphenyl)propane,  
1,4-bis[1'-(4''-aminophenyl)-1'-methylethyl]benzene,  
1,3-bis[1'-(4''-aminophenyl)-1'-methylethyl]benzene,  
bis(2-dimethylaminoethyl)ether,  
bis(2-diethylaminoethyl)ether, and the like.

As examples of the nitrogen-containing compounds (c),  
polyethyleneimine, polyallylamine, a polymer of  
2-dimethylaminoethylacrylamide, and the like can be given.

As examples of the quaternary ammonium hydroxide compound,  
tetramethylammonium hydroxide, tetraethylammonium hydroxide,  
tetra-n-propylammonium hydroxide, tetra-n-butylammonium  
hydroxide, and the like can be given.

[0135]

Examples of the amide group-containing compound include,  
in addition to N-t-butoxycarbonyl group-containing amino  
compounds such as N-t-butoxycarbonyl di-n-octylamine,  
N-t-butoxycarbonyl di-n-nonylamine, N-t-butoxycarbonyl  
di-n-decylamine, N-t-butoxycarbonyl dicyclohexylamine,  
N-t-butoxycarbonyl-1-adamantylamine, N-t-butoxycarbonyl-N-  
methyl-1-adamantylamine,

N,N-di-t-butoxycarbonyl-1-adamantylamine,  
 N,N-di-t-butoxycarbonyl-N-methyl-1-adamantylamine,  
 N-t-butoxycarbonyl-4,4'-diaminodiphenylmethane,  
 N,N'-di-t-butoxycarbonylhexamethylenediamine,  
 N,N,N',N'-tetra-t-butoxycarbonylhexamethylenediamine,  
 N,N'-di-t-butoxycarbonyl-1,7-diaminoheptane,  
 N,N'-di-t-butoxycarbonyl-1,8-diaminooctane,  
 N,N'-di-t-butoxycarbonyl-1,9-diaminononane,  
 N,N'-di-t-butoxycarbonyl-1,10-diaminodecane,  
 N,N'-di-t-butoxycarbonyl-1,12-diaminododecane,  
 N,N'-di-t-butoxycarbonyl-4,4'-diaminodiphenylmethane,  
 N-t-butoxycarbonylbenzimidazole,  
 N-t-butoxycarbonyl-2-methylbenzimidazole, and  
 N-t-butoxycarbonyl-2-phenylbenzimidazole, formamide,  
 N-methylformamide, N,N-dimethylformamide, acetamide,  
 N-methylacetamide, N,N-dimethylacetamide, propionamide,  
 benzamide, pyrrolidone, N-methylpyrrolidone and the like.

[0136]

As examples of the urea compounds, urea, methylurea,  
 1,1-dimethylurea, 1,3-dimethylurea, 1,1,3,3-tetramethylurea,  
 1,3-diphenylurea, tri-n-butylthiourea, and the like can be  
 given.

Examples of the nitrogen-containing heterocyclic  
 compounds include: imidazoles such as imidazole, benzimidazole,  
 4-methylimidazole, and 4-methyl-2-phenylimidazole; pyridines  
 such as pyridine, 2-methylpyridine, 4-methylpyridine,  
 2-ethylpyridine, 4-ethylpyridine, 2-phenylpyridine,

4-phenylpyridine, 2-methyl-4-phenylpyridine, nicotine, nicotinic acid, nicotinamide, quinoline, 4-hydroxyquinoline, 8-oxyquinoline, and acridine; piperazines such as piperazine, 1-(2'-hydroxyethyl)piperazine; pyrazine, pyrazole, pyridazine, quinoxaline, purine, pyrrolidine, piperidine, 3-piperidino-1,2-propanediol, morpholine, 4-methylmorpholine, 1,4-dimethylpiperazine, and 1,4-diazabicyclo[2.2.2]octane; and the like.

[0137]

Of these nitrogen-containing organic compounds, the nitrogen-containing compounds (a), nitrogen-containing compounds (b), quaternary ammonium hydroxide compounds, nitrogen-containing heterocyclic compounds, and the like are preferable.

The acid diffusion controller may be used either individually or in combination of two or more.

The amount of the acid diffusion controller to be added is usually 15 parts by weight or less, preferably 10 parts by weight or less, and still more preferably 5 parts by weight or less for 100 parts by weight of the resin (A). If the proportion of the acid diffusion controller exceeds 15 parts by weight, sensitivity as a resist and developability of the exposed area tend to decrease. If the amount is less than 0.001 part by weight, the pattern shape or dimensional accuracy as a resist may decrease depending on the processing conditions.

[0138]

Alicyclic additives which further improve dry etching

resistance, pattern shape, adhesion to substrate, or the like may be added to the radiation-sensitive resin composition of the present invention.

Examples of such alicyclic additives include:  
adamantane derivatives such as t-butyl  
1-adamantanecarboxylate, t-butoxycarbonylmethyl  
1-adamantanecarboxylate, di-t-butyl  
1,3-adamantanedicarboxylate, t-butyl 1-adamantaneacetate,  
t-butoxycarbonylmethyl 1-adamantaneacetate, and di-t-butyl  
1,3-adamantanediacetate;  
deoxycholates such as t-butyl deoxycholate,  
t-butoxycarbonylmethyl deoxycholate, 2-ethoxyethyl  
deoxycholate, 2-cyclohexyloxyethyl deoxycholate,  
3-oxocyclohexyl deoxycholate, tetrahydropyranyl deoxycholate,  
and mevalonolactone deoxycholate;  
lithocholates such as t-butyl lithocholate,  
t-butoxycarbonylmethyl lithocholate, 2-ethoxyethyl  
lithocholate, 2-cyclohexyloxyethyl lithocholate,  
3-oxocyclohexyl lithocholate, tetrahydropyranyl lithocholate,  
and mevalonolactone lithocholate;  
2,5-dimethyl-2,5-di(adamantylcarbonyloxy)hexane; and the  
like.

These alicyclic additives may be used either individually or in combination of two or more.

The amount of the alicyclic additives to be added is usually 50 parts by weight or less, and preferably 30 parts by weight or less for 100 parts by weight of the resin (A). If the

amount of alicyclic additives exceeds 50 parts by weight, heat resistance as a resist tends to decrease.

[0139]

Surfactants which improve applicability, developability, or the like may be added to the radiation-sensitive resin composition of the present invention.

As examples of surfactants, nonionic surfactants such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene n-octyl phenyl ether, polyoxyethylene n-nonyl phenyl ether, polyethylene glycol dilaurate, polyethylene glycol distearate; commercially available products such as KP341 (manufactured by Shin-Etsu Chemical Co., Ltd.), Polyflow No. 75, No. 95 (manufactured by Kyoeisha Chemical Co., Ltd.), FTOP EF301, EF303, EF352 (manufactured by TOHKEM PRODUCTS CORPORATION), MEGAFAC F171, F173 (manufactured by Dainippon Ink and Chemicals, Inc.), Florard FC430, FC431 (manufactured by Sumitomo 3M Ltd.), Asahi Guard AG710, Surflon S-382, SC-101, SC-102, SC-103, SC-104, SC-105, SC-106 (manufactured by Asahi Glass Co., Ltd.); and the like can be given.

These surfactants may be used either individually or in combination of two or more.

The amount of surfactants to be added is usually 2 parts by weight or less for 100 parts by weight of the total of the resin (A) and the acid generator (B).

As other additives, halation inhibitors, adhesion promoters, storage stabilizers, anti-foaming agents, and the

like can be given.

[0140]

#### Preparation of composition solution

The radiation-sensitive resin composition of the present invention is prepared as a composition solution by dissolving the composition in a solvent so that the total solid content is 5-50 wt%, and preferably 10-25 wt%, and filtering the composition using a filter with a pore diameter of about 0.2  $\mu\text{m}$ , for example.

Examples of solvents used for preparation of the composition solution include:

linear or branched ketones such as 2-butanone, 2-pentanone, 3-methyl-2-butanone, 2-hexanone, 4-methyl-2-pentanone, 3-methyl-2-pentanone, 3,3-dimethyl-2-butanone, 2-heptanone, and 2-octanone;

cyclic ketones such as cyclopentanone, 3-methylcyclopentanone, cyclohexanone, 2-methylcyclohexanone, 2,6-dimethylcyclohexanone, and isophorone;

propylene glycol monoalkyl ether acetates such as propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol mono-n-propyl ether acetate, propylene glycol mono-i-propyl ether acetate, propylene glycol mono-n-butyl ether acetate, propylene glycol mono-i-butyl ether acetate, propylene glycol mono-sec-butyl ether acetate, and propylene glycol mono-t-butyl ether acetate;

alkyl 2-hydroxypropionates such as methyl 2-hydroxypropionate, ethyl 2-hydroxypropionate, n-propyl 2-hydroxypropionate,



i-propyl 2-hydroxypropionate, n-butyl 2-hydroxypropionate, i-butyl 2-hydroxypropionate, sec-butyl 2-hydroxypropionate, and t-butyl 2-hydroxypropionate;  
alkyl 3-alkoxypropionates such as methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, and ethyl 3-ethoxypropionate;

[0141]

as well as other solvents such as n-propyl alcohol, i-propyl alcohol, n-butyl alcohol, t-butyl alcohol, cyclohexanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol di-n-propyl ether, diethylene glycol di-n-butyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol mono-n-propyl ether acetate, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-n-propyl ether, toluene, xylene, 2-hydroxy-2-methylethyl propionate, ethoxyethyl acetate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutyrate, 3-methoxybutylacetate, 3-methyl-3-methoxybutylacetate, 3-methyl-3-methoxybutylpropionate, 3-methyl-3-methoxybutylbutyrate, ethyl acetate, n-propyl acetate, n-butylacetate, methyl acetoacetate, ethyl acetoacetate, methyl pyruvate, ethyl pyruvate, N-methyl pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, benzyl ethyl ether, di-n-hexyl ether, diethylene glycol

monomethyl ether, diethylene glycol monoethyl ether, caproic acid, caprylic acid, 1-octanol, 1-nonanol, benzyl alcohol, benzyl acetate, ethyl benzoate, diethyl oxalate, diethyl maleate,  $\gamma$ -butyrolactone, ethylene carbonate, propylene carbonate, and the like.

[0142]

These solvents may be used either individually or in combination of two or more. Among these solvents, linear or branched ketones, cyclic ketones, propylene glycol monoalkyl ether acetates, alkyl 2-hydroxypropionates, and alkyl 3-alkoxypropionates are preferable.

[0143]

#### Formation of resist pattern

The radiation-sensitive resin composition of the present invention is particularly useful as a chemically-amplified resist.

In the chemically-amplified resist, an acid-dissociable group in the resin (A) dissociates by the action of an acid generated from the acid generator (B) upon exposure, thereby producing an acidic functional group, preferably a carboxyl group. As a result, solubility of the exposed part of the resist in an alkaline developer increases, whereby the exposed part is dissolved in an alkaline developer and removed to obtain a positive-tone resist pattern.

A resist pattern is formed from the radiation-sensitive resin composition of the present invention by applying the composition solution to, for example, substrates such as a

silicon wafer or a wafer coated with aluminum using an appropriate application method such as rotational coating, cast coating, and roll coating to form a resist film. The resist film is then optionally pre-baked (hereinafter called "PB") and exposed to form a predetermined resist pattern. As radiation used for exposure, visible rays, ultraviolet rays, deep ultraviolet rays, X-rays, electron beams, or the like is appropriately selected depending on types of the acid generator. It is particularly preferable to use an ArF excimer laser (wavelength: 193 nm) or KrF excimer laser (wavelength: 248 nm).

In the present invention, it is preferable to perform post-exposure bake (hereinafter called "PEB"). PEB ensures smooth dissociation of the acid-dissociable organic group in the resin (A). The heating temperature for PEB is usually 30-200°C, and preferably 50-170°C, although the heating conditions vary depending on the composition of the radiation-sensitive resin composition.

[0144]

In order to bring out latent capability of the radiation-sensitive resin composition of the present invention, an organic or inorganic anti-reflection film may be formed on a substrate as disclosed in Japanese Patent Publication No. 12452/1994, for example. Moreover, a protection film may be formed on the resist film as disclosed in Japanese Patent Publication No. 188598/1993 or the like in order to prevent the effects of basic impurities or the like in an environmental atmosphere. These techniques may be employed in combination.

The exposed resist film is then developed to form a predetermined resist pattern.

As examples of a developer used for development, it is preferable to use an alkaline aqueous solution prepared by dissolving at least one of alkaline compounds such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate, aqueous ammonia, ethylamine, n-propylamine, diethylamine, di-n-propylamine, triethylamine, methyldiethylamine, ethyldimethylamine, triethanolamine, tetramethylammonium hydroxide, pyrrole, piperidine, choline, 1,8-diazabicyclo-[5.4.0]-7-undecene, and 1,5-diazabicyclo-[4.3.0]-5-nonene.

The concentration of the alkaline aqueous solution is usually 10 wt% or less. If the concentration of the alkaline aqueous solution exceeds 10 wt%, an unexposed area may be dissolved in the developer.

[0145]

Organic solvents or the like may be added to the developer containing an alkaline aqueous solution.

As examples of organic solvents, linear, branched, or cyclic ketones such as acetone, methyl ethyl ketone, methyl i-butyl ketone, cyclopentanone, cyclohexanone, 3-methylcyclopentanone, and 2,6-dimethylcyclohexanone; alcohols such as methylalcohol, ethylalcohol, n-propylalcohol, i-propylalcohol, n-butylalcohol, t-butylalcohol, cyclopentanol, cyclohexanol, 1,4-hexanediol, and 1,4-hexanedimethylol; ethers such as tetrahydrofuran and

dioxane; esters such as ethyl acetate, n-butyl acetate, and i-amyl acetate; aromatic hydrocarbons such as toluene and xylene; phenol, acetonylacetone, dimethylformamide; and the like can be given.

These organic solvents may be used either individually or in combination of two or more.

The amount of the organic solvents is preferably 100 vol% or less of the alkaline aqueous solution. If the amount of the organic solvents exceeds 100 vol%, an exposed area may remain undeveloped due to decreased developability.

In addition, surfactants or the like may be added to the developer containing the alkaline aqueous solution in an appropriate amount.

The resist film is generally washed with water after development using a developer containing an alkaline aqueous solution.

[0146]

[Preferred Embodiment of the Invention]

The embodiments of the present invention are described in more detail by examples. However, these examples should not be construed as limiting the present invention. In the examples, part(s) refers to part(s) by weight unless otherwise indicated.

Measurement and evaluation of each composition in the examples and comparative examples were carried out as follows.

Mw:

Mw was measured by gel permeation chromatography (GPC) using GPC columns (manufactured by Tosoh Corp., G2000HXL x 2,

G3000HXL x 1, G4000HXL x 1) under the following conditions.  
Flow rate: 1.0 ml/minute, eluate: tetrahydrofuran, column  
temperature: 40°C, standard reference material: monodispersed  
polystyrene.

Radiation transmittance:

A solution composition was applied to a quartz plate and the coating was post-baked on a hot plate at 90°C for 60 seconds to obtain a resist coating with a thickness of 1 µm. Radiation transmittance of the resist coating was calculated from absorbance at a wavelength of 193 nm and was adopted as a standard for transparency in the deep UV ray region.

[0147]

Sensitivity (Examples 1-18 and Comparative Example 1):

A solution composition with a formulation shown in Table 1 was applied to a silicon wafer (ARC) with a 520Å thickness Deep UV30 film (manufactured by Brewer Science Corp.) formed on the surface by spin coating and post-baked on a hot plate under the conditions shown in Table 2 to obtain a resist coating with a thickness of 0.4 µm.

The coating was exposed to radiation through a mask pattern using an ArF excimer laser exposure apparatus (manufactured by Nikon Corp., lens numerical aperture: 0.55, wavelength: 193 nm). After PEB under the conditions shown in Table 2, the resist coatings were developed in a 2.38 wt% tetramethylammonium hydroxide aqueous solution (Examples 1-18) or 2.38 x 1/50 wt% tetramethylammonium hydroxide aqueous solution (Comparative Example 1) at 25°C for 1 minute, washed with water, and dried

to form a positive-tone resist pattern. An optimum dose at which a line-and-space (1L1S) pattern with a line width of 0.18  $\mu\text{m}$  was formed was taken as sensitivity.

#### Sensitivity (Example 19)

A solution composition with a formulation shown in Table 1 was applied to a silicon wafer (AR-19) manufactured by Shipley Corp. by spin coating and post-baked on a hot plate under the conditions shown in Table 2 to obtain a resist coating with a thickness of 0.4  $\mu\text{m}$ .

The coating was exposed to radiation through a mask pattern using an ISI mini-stepper (lens numerical aperture: 0.60, wavelength: 193 nm). After performing PEB under the conditions shown in Table 2, the resist films were developed in a 2.38 wt% tetramethylammonium hydroxide aqueous solution at 25°C for 1 minute, washed with water, and dried to form a positive-tone resist pattern. An optimum dose capable of forming a 1:1 line width from a line-and-space (1L1S) pattern with a line width of 0.15  $\mu\text{m}$  was taken as sensitivity.

[0148]

#### Resolution:

Minimum dimensions of the resist pattern resolved at the optimum dose were taken as the resolution.

#### Defective development:

Defective development was evaluated by observing the presence or absence of the defective development using an optical microscope and a KLA defect inspection device (manufactured by KLA-TENCOR JAPAN LTD.) by the following

procedure.

Evaluation procedure using KLA defect inspection device:

The total number of defective clusters and unclusters in one piece of wafer extracted from the difference produced by superposing reference images and pixels was counted by array mode observation using the KLA defect inspection device of which the sensitivity was set to detect defects with a size  $0.15\text{ }\mu\text{m}$  or greater.

Pattern configuration:

The dimensions of the lower side  $L_1$  and the upper side  $L_2$  of the rectangular cross-section of a line and space pattern (1L1S) with a line width of  $0.20\text{ }\mu\text{m}$  were measured using a scanning electron microscope. A pattern configuration which satisfied a formula " $0.85 \leq L_2/L_1 \leq 1$ " and was straight with no extended skirt was evaluated as "Good", and otherwise evaluated as "Bad".

[0149]

Synthesis of monomers

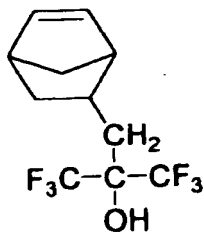
Synthesis Example 1

A 500 ml autoclave was charged with 22 g of cyclopentadiene, 109 g of 1,1-bis(trifluoromethyl)-3-butenol, and 450 mg of hydroquinone in an argon atmosphere, and the mixture was heated at  $170^\circ\text{C}$  for 17 hours. The reaction solution was distilled to obtain 70 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene of the following formula (11).

[0150]

[Chemical Formula 39]





(11)

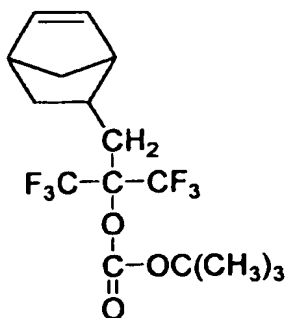
[0151]

#### Synthesis Example 2

A 500 ml reaction vessel was charged with 10 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene obtained in Synthesis Example 1, 10 g of potassium carbonate, 40 g of tetrahydrofuran, and 20 g of water. After the addition of 8 g of t-butyl bromoacetate, the mixture was reacted at 70°C for six hours. The reaction mixture was mixed with 200 ml of ethyl acetate and the mixture was washed with water. The solvent was removed under reduced pressure to obtain a crude product. The crude product was distilled under reduced pressure to obtain 7 g of 5-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene of the following formula (12).

[0152]

[Chemical Formula 40]



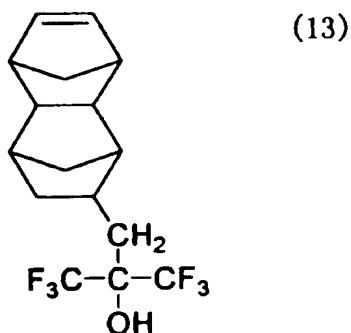
[0153]

### Synthesis Example 3

A 500 ml autoclave was charged with 230 g of 1,1-bis(trifluoromethyl)-3-butenol, 73 g of dicyclopentadiene, and 0.15 g of 2,6-di-*t*-butylparacresol, and the mixture was heated at 190°C for 12 hours. The reaction solution was cooled to room temperature and purified by distillation to obtain 40 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl) tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene of the following formula (13).

[0154]

[Chemical Formula 41]



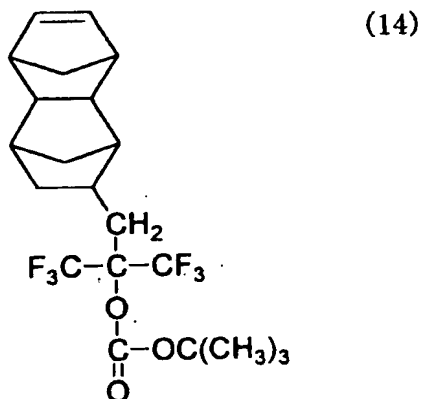
[0155]

Synthesis Example 4

6 g of 8-[2,2-bis(trifluoromethyl)-2-t-butoxy-carbonyloxyethyl]tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene of the following formula (14) was prepared in the same manner as in the Synthesis Example 2 except for using 10 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene obtained in the Synthesis Example 3 instead of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene.

[0156]

[Chemical Formula 42]



[0157]

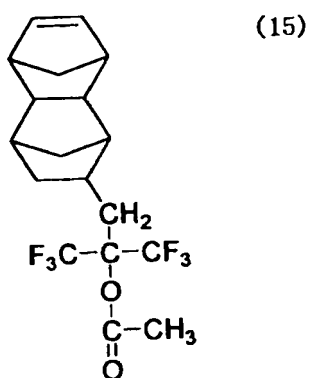
Synthesis Example 5

10 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene obtained

in the Synthesis Example 3 was refluxed for 24 hours in acetic anhydride and the crude product obtained was purified by distillation to obtain 6 g of 8-[2,2-bis(trifluoromethyl)-2-methylcarbonyloxyethyl]tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene of the following formula (15).

[0158]

[Chemical Formula 43]



[0159]

#### Synthesis of resin (A)

##### Synthesis Example 6

A 100 ml pressure polymerization bottle was charged with 15 ml of 1,2-dichloroethane, 4.5 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene, and 2.4 g of 5-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene. 2 ml of a solution of palladium complex catalyst prepared by the method described below was added to initiate the polymerization reaction. The reaction was continued for 6 hours at 30°C. The reaction solution was charged into a large amount of methanol

to coagulate the product, which was filtered to obtain 4.7 g of a resin.

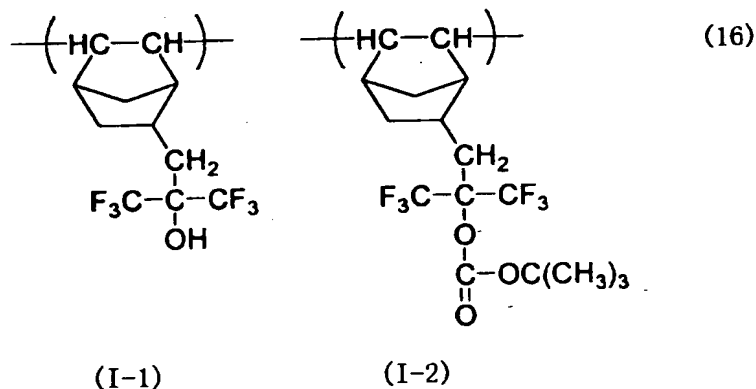
The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1) and recurring unit (I-2), shown in the following formulas (16), of 65:35, and having Mw of 6,000. This resin is referred to as a "resin (A-1)".

<Preparation of catalyst>

A solution of 40 mg of silver hexafluoroantimonate dissolved in 1 ml of 1,2-dichloroethane was added to a solution of 27 mg of  $\pi$ -allyl palladium chloride dimer in 1 ml of 1,2-dichloroethane. The mixture was stirred for one hour at room temperature and silver chloride formed was separated by filtration to obtain a solution of palladium complex catalyst in 1,2-dichloroethane.

[0160]

[Chemical Formula 44]



[0161]

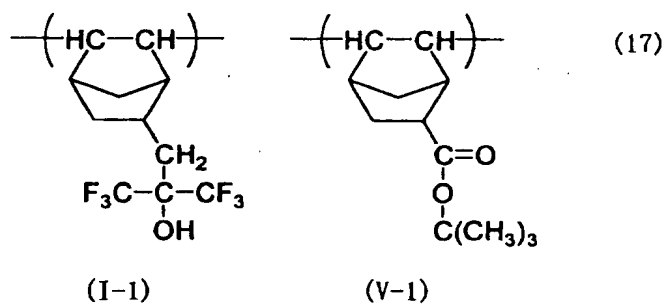
### Synthesis Example 7

The same polymerization reaction as in the Synthesis Example 6 was carried out, except for using 5.4 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene and 2.1 g of 5-t-butoxycarbonylbicyclo[2.2.1]hept-2-ene as monomers, to obtain 5.1 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1) and recurring unit (V-1), shown in the following formulas (17), of 65:35, and having Mw of 6,200. This resin is referred to as a "resin (A-2)".

[0162]

[Chemical Formula 45]



[0163]

### Synthesis Example 8

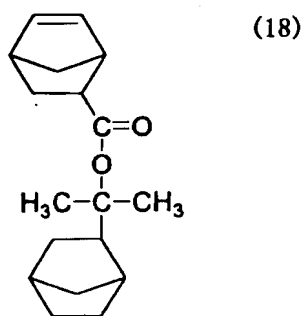
The same polymerization reaction as in the Synthesis Example 6 was carried out, except for using 4.9 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene and 2.6 g of the compound shown by the following

formula (18) as monomers, to obtain 4.9 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1) and recurring unit (V-2), shown in the following formulas (19), of 65:35, and having Mw of 5,800. This resin is referred to as a "resin (A-3)".

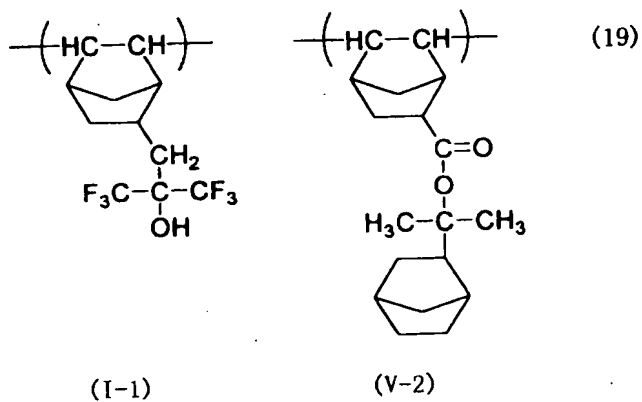
[0164]

[Chemical Formula 46]



[0165]

[Chemical Formula 47]



[0166]

#### Synthesis Example 9

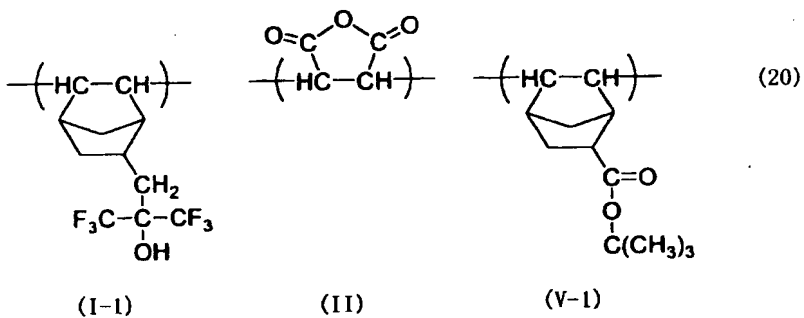
A 100 ml eggplant flask was charged with 12.1 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene, 5.7 g of 5-t-butoxycarbonylbicyclo[2.2.1]hept-2-ene, 7.2 g of maleic anhydride, 1.5 g of azobisisobutyronitrile, and 25 g of tetrahydrofuran in a nitrogen atmosphere. The mixture was polymerized at 60°C for eight hours. After polymerization, the reaction solution was cooled to room temperature and poured into a large quantity of a i-propylalcohol/n-hexane mixed solution to coagulate the resin. The coagulated resin was filtered, washed with a small amount of n-hexane, and dried under vacuum to obtain 20 g of a resin product.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1), recurring unit (II), and recurring unit (V-1), shown in the following formulas (20), of 30:20:50, and having Mw of 7,000. This resin is referred to as a "resin (A-4)".

[0167]

[Chemical Formula 48]





[0168]

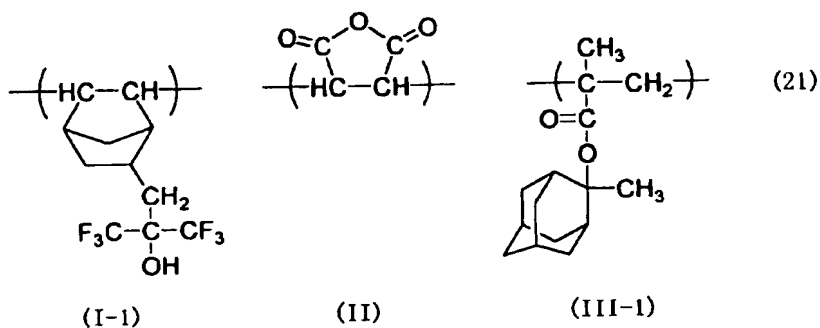
#### Synthesis Example 10

The same polymerization reaction as in the Synthesis Example 9. was carried out, except for using 12 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene, 4.3 g of maleic anhydride, and 8.7 g of 2-(2-methyl)adamantyl methacrylate as monomers, to obtain 19 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1), recurring unit (II), and recurring unit (III-1), shown in the following formulas (21), of 35:35:30, and having Mw of 6,800. This resin is referred to as a "resin (A-5)".

[0169]

[Chemical Formula 49]



[0170]

#### Synthesis Example 11

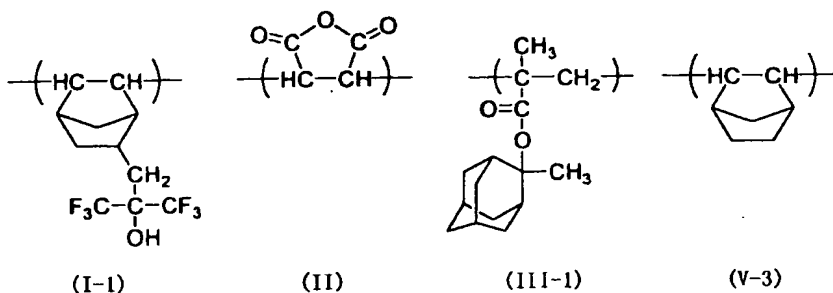
The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 11.5 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene, 1.3 g of norbornene, 5.5 g of maleic anhydride, and 6.6 g of 2-(2-methyl)adamantyl methacrylate as monomers, to obtain 21 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1), recurring unit (II), recurring unit (III-1), and recurring unit (V-3), shown in the following formulas (22), of 30:10:40:20, and having Mw of 7,300. This resin is referred to as a "resin (A-6)".

[0171]

[Chemical Formula 50]

(22)



[0172]

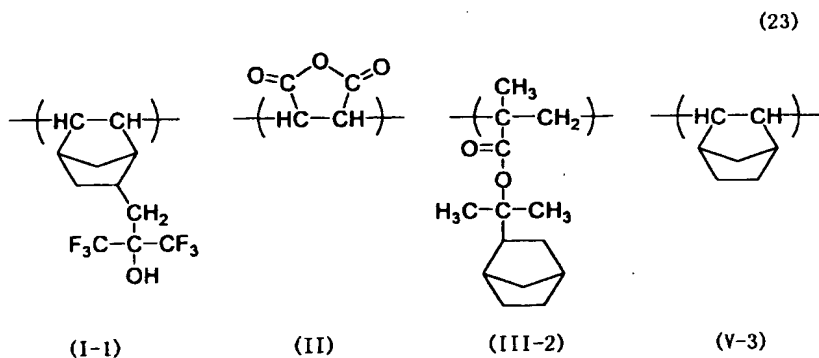
#### Synthesis Example 12

The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 11.8 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene, 1.4 g of norbornene, 5.6 g of maleic anhydride, and 6.4 g of 2-(2'-methacryloyloxy-2'-propyl)norbornene as monomers, to obtain 20 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1), recurring unit (II), recurring unit (III-2), and recurring unit (V-3), shown in the following formulas (23), of 30:10:40:20, and having Mw of 6,400. This resin is referred to as a "resin (A-7)".

[0173]

[Chemical Formula 51]



[0174]

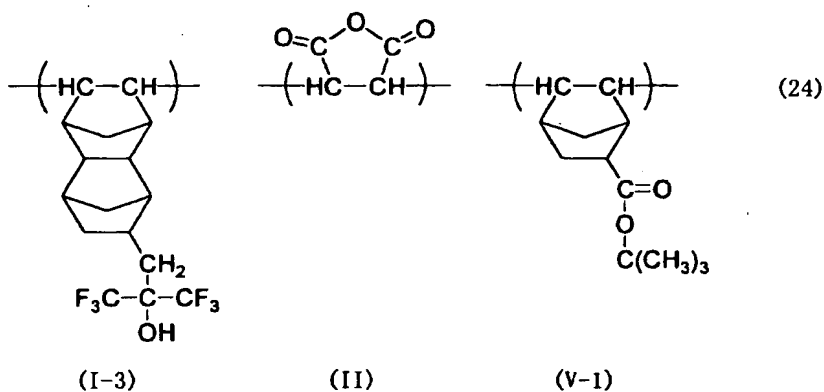
### Synthesis Example 13

The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 9.7 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl) tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 8.3 g of 5-t-butoxycarbonylbicyclo[2.2.1]hept-2-ene, and 7 g of maleic anhydride as monomers, to obtain 21 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-3), recurring unit (II), and recurring unit (V-1), shown in the following formulas (24), of 30:20:50, and having Mw of 7,100. This resin is referred to as a "resin (A-8)".

[0175]

[Chemical Formula 52]



[0176]

#### Synthesis Example 14

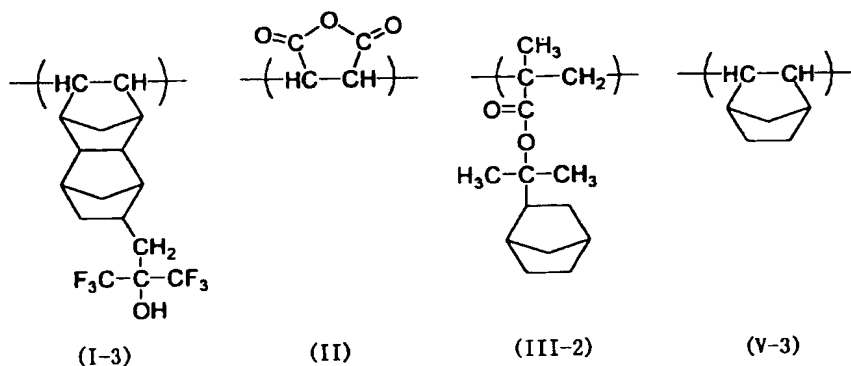
The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 12.3 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl) tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 0.6 g of norbornene, 4.2 g of maleic anhydride, and 8 g of 2-(2'-methacryloyloxy-2'-propyl)norbornene as monomers, to obtain 22 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-3), recurring unit (II), recurring unit (III-2), and recurring unit (V-3), shown in the following formulas (25), of 30:10:40:20, and having Mw of 6,500. This resin is referred to as a "resin (A-9)".

[0177]

[Chemical Formula 53]

(25)



[0178]

## Synthesis Example 15

## (1) Polymerization

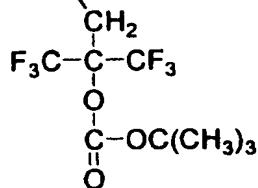
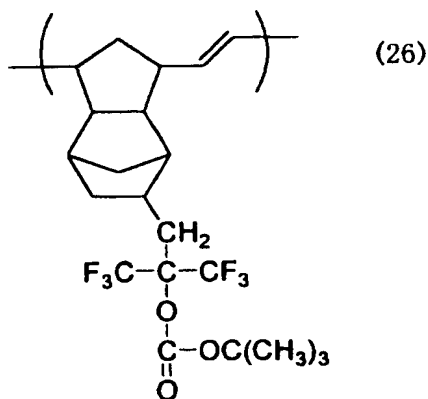
A separable flask equipped with a stirrer, a reflux condenser, and a three-way cock was charged with 100 parts by weight of 8-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 33 parts by weight of 1-hexene (molecular weight modifier), and 200 parts by weight of toluene, and the mixture was heated to 80°C. Next, after the addition of 0.17 part by weight of a toluene solution of triethylaluminum (concentration: 1.5 mol/l) and 1.0 part by weight of a toluene solution of tungsten hexachloride (concentration: 0.05 mol/l) as a metathesis catalyst, the ring-opening polymerization reaction was carried out at 80°C for three hours while stirring to obtain a resin solution.

The resin was confirmed to be a polymer consisting of the recurring unit (IV-1) of the following formula (26) and having

Mw of 12,000 (yield 67 wt%). This resin is referred to as a "resin (A-10)".

[0179]

[Chemical Formula 54]



[0180]

## (2) Hydrogenation

An autoclave was charged with 400 parts by weight of resin (A-10) and 0.075 part by weight of chlorohydrocarbonyltriphenylphosphine ruthenium as a hydrogenation catalyst. Hydrogenation reaction was carried out at 165°C under a hydrogen pressure of 100 kg/cm<sup>2</sup> · G for four hours.

400 parts by weight of the resulting reaction solution and 100 parts by weight of toluene were charged to another reaction vessel. After the addition of 0.71 part by weight of lactic acid and 1.15 parts by weight of water, the mixture was stirred

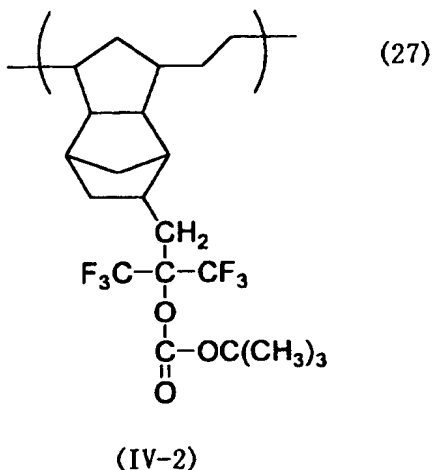
at 60°C for 30 minutes. Then, after further addition of 260 parts of methanol, the mixture was further stirred at 60°C for one hour. The reaction solution was cooled to room temperature and separated into a poor solvent layer (methanol layer) and a good solvent layer (resin solution layer). Only the poor solvent layer was removed. Methanol and toluene in the amount equivalent to 4.5 wt% and 55 wt% of the removed methanol, respectively, were added to the reaction vessel, and the mixture was stirred at 60°C for one hour. Then, the reaction solution was again cooled to room temperature and separated into a poor solvent layer and a good solvent layer to remove only the poor solvent layer. This extraction procedure using methanol was repeated several times. The good solvent was removed from the finally obtained good solvent layer by evaporation, thereby collecting the resin. The resin was re-dissolved in tetrahydrofuran and a large amount of methanol was added to coagulate the resin. The coagulated resin was dried under reduced pressure to obtain a resin.

The degree of hydrogenation determined by the NMR spectrum was 100% and the resin was confirmed to be a polymer consisting of the recurring unit (IV-2) of the following formula (27). This resin is referred to as a "resin (A-11)".

[0181]

[Chemical Formula 55]





[0182]

### (3) Hydrolysis:

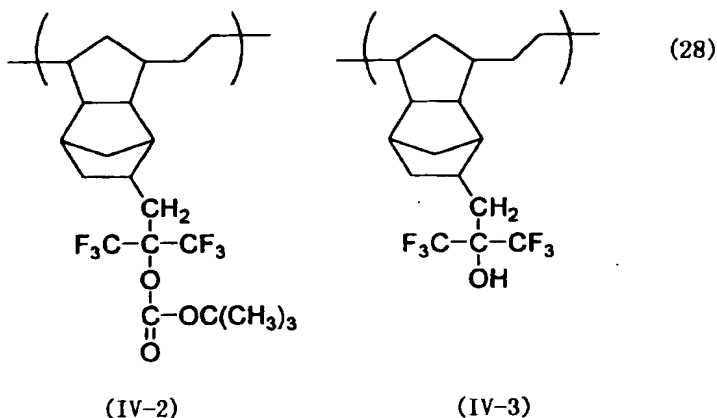
A flask was charged with 100 parts by weight of the resin (A-11), 200 parts by weight of propylene glycol monomethyl ether, 100 parts by weight of distilled water, and 1 part by weight of p-toluenesulfonic acid. Hydrolysis reaction was carried out for 8 hours while refluxing in a nitrogen atmosphere. The reaction solution was cooled to room temperature and neutralized by the addition of a large amount of water and triethylamine. The resin was extracted using ethyl acetate and the extracted resin solution layer was washed with water until the water layer became neutral. The solvent was evaporated to obtain a resin.

The degree of hydrolysis determined by IR spectrum was 60%, and the resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (IV-2) and recurring unit (IV-3), shown in the following formulas (28),

of 40:60. This resin is referred to as a "resin (A-12)".

[0183]

[Chemical Formula 56]



[0184]

#### Synthesis Example 16

##### (1) Polymerization

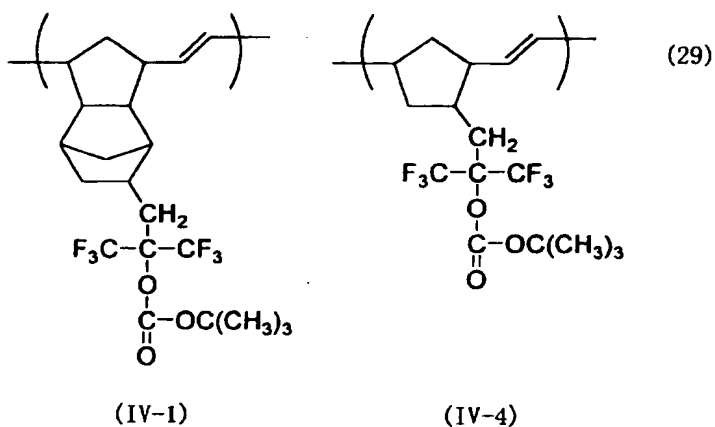
A separable flask equipped with a stirrer, a reflux condenser, and a three-way cock was charged with 60 parts by weight of 8-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 40 parts by weight of 5-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene, 25 parts by weight of 1-hexene (molecular weight modifier), 400 parts by weight of 1,2-dichloroethane, and 0.6 part by weight of a chlorobenzene solution of triethylaluminum (concentration: 1.5 mol/l) and 4 parts by weight of a chlorobenzene solution of tungsten hexachloride (concentration: 10.025 mol/l) as a

metathesis catalyst. The ring-opening polymerization reaction was carried out at 80°C for three hours. After the polymerization reaction, a large amount of methanol was added to the reaction solution to cause the resin to coagulate. The coagulated resin was filtered and dried under vacuum to obtain a resin (yield: 92 wt%).

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (IV-1) and recurring unit (IV-4), shown in the following formulas (29), of 50:50, and having Mw of 13,000. This resin is referred to as a "resin (A-13)".

[0185]

[Chemical Formula 57]



[0186]

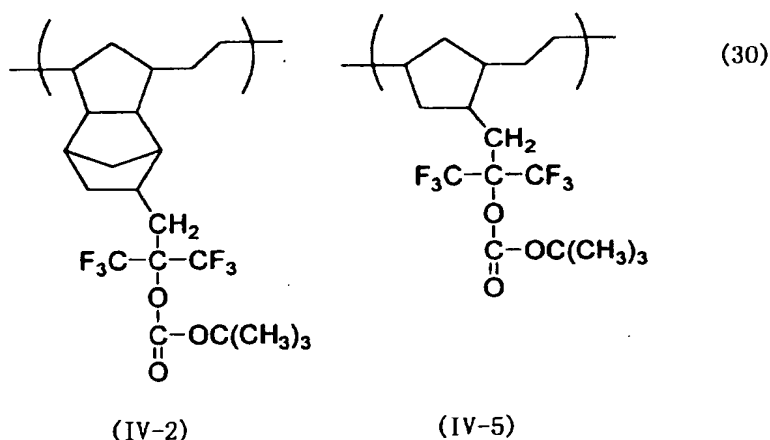
## (2) Hydrogenation

A hydrogenation reaction was carried out in the same manner as in Synthesis Example 15 using the resin (A-13).

The degree of hydrogenation determined by the IR spectrum and NMR spectrum was 100% and the resin was confirmed to be a copolymer consisting of the recurring unit (IV-2) and recurring unit (IV-5) of the following formula (30). This resin is referred to as a "resin (A-14)".

[0187]

[Chemical Formula 58]



[0188]

### (3) Hydrolysis:

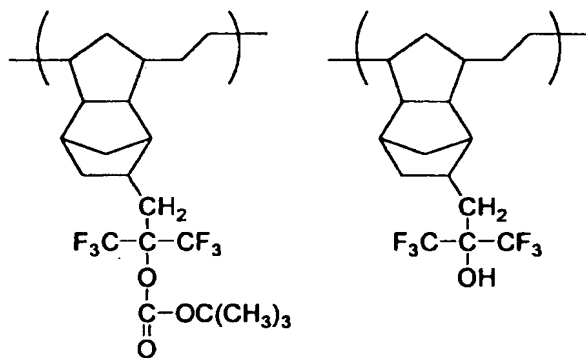
A hydrolysis reaction was carried out in the same manner as in Synthesis Example 15 using the resin (A-14).

The degree of hydrolysis determined by IR spectrum was 70%, and the resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (IV-2), recurring unit (IV-3), recurring unit (IV-5), and recurring unit (IV-6), shown in the following formulas (31), of 13:37:17:33. This resin is referred to as a "resin (A-15)".

[0189]

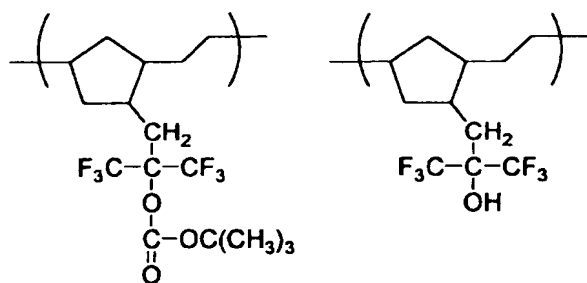
[Chemical Formula 59]

(31)



(IV-2)

(IV-3)



(IV-5)

(IV-6)

[0190]

#### Synthesis Example 17

##### (1) Polymerization

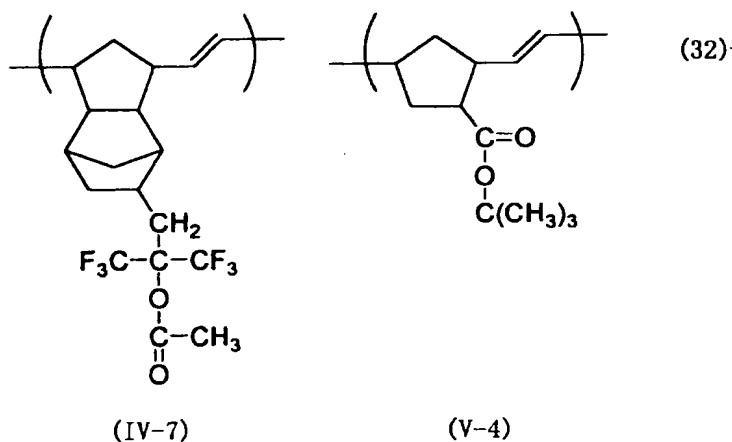
The same ring-opening polymerization reaction as in the Synthesis Example 16 was carried out, except for using 50 parts by weight of 8-[2,2-bis(trifluoromethyl)-2-methylcarbonyloxyethyl]tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-

ene and 50 parts by weight of  
5-t-butoxycarbonylbicyclo[2.2.1]hept-2-ene.

The resulting resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (IV-7) and recurring unit (V-4), shown in the following formulas (32), of 40:60, and having Mw of 13,000. This resin is referred to as a "resin (A-16)".

[0191]

[Chemical Formula 60]



[0192]

## (2) Hydrogenation

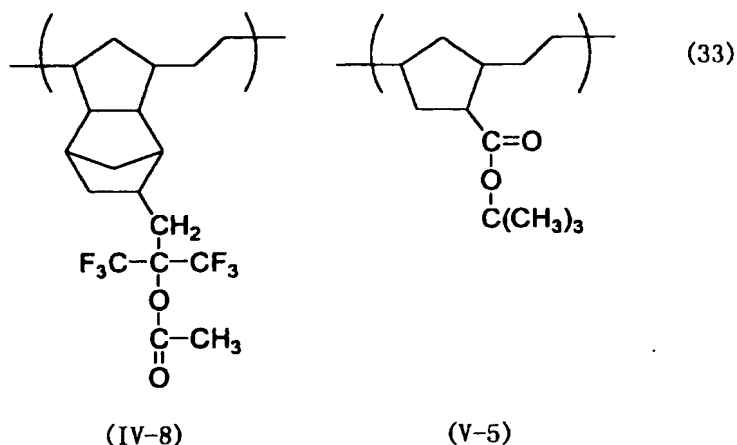
A hydrogenation reaction was carried out in the same manner as in Synthesis Example 15 using the resin (A-16).

The degree of hydrogenation determined by the IR spectrum and NMR spectrum was 100% and the resin was confirmed to be a copolymer consisting of the recurring unit (IV-8) and recurring unit (V-5) of the following formula (33). This resin is

referred to as a "resin (A-17)".

[0193]

[Chemical Formula 61]



[0194]

### (3) Hydrolysis:

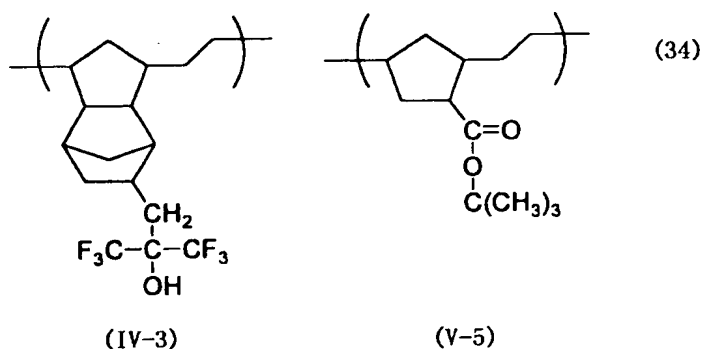
A flask was charged with 100 parts by weight of the resin (A-17), 500 parts by weight of tetrahydrofuran, 50 parts by weight of an aqueous solution of potassium hydroxide (concentration: 10 mol/l), and the hydrolysis reaction was carried out for 6 hours while refluxing in a nitrogen atmosphere. The reaction solution was cooled to room temperature and neutralized by the addition of a large amount of water and oxalic acid. The resin was extracted using methyl acetate and the extracted resin solution layer was washed with water until the water layer became neutral. The solvent was evaporated to obtain a resin.

The degree of hydrolysis of methylcarbonyloxy groups

determined by the IR spectrum was 100% and the resin was confirmed to be a copolymer consisting of the recurring unit (IV-3) and recurring unit (V-5) of the following formula (34). This resin is referred to as a "resin (A-18)".

[0195]

[Chemical Formula 62]



[0196]

#### Synthesis Example 18

The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 5.81 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene, 14.00 g of 5-[2,2-bis(trifluoromethyl)-2-tert-butoxycarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene, and 5.19 g of maleic anhydride as monomers, to obtain 16 g of a resin.

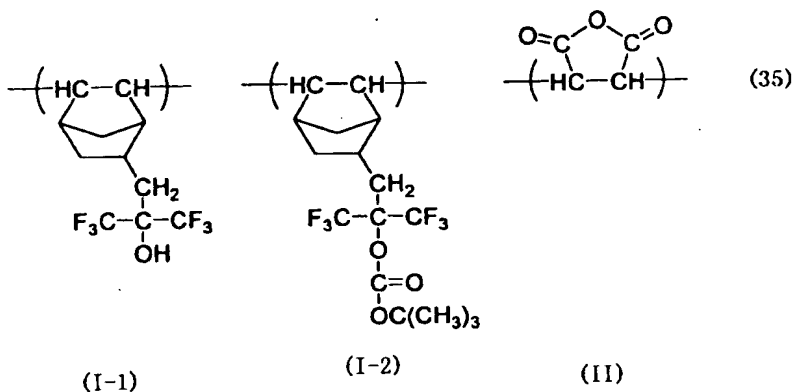
The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1), recurring unit (I-2), and recurring unit (II), shown in the following formulas (35), of 20:30:50, and having Mw of 4,500.



This resin is referred to as a "resin (A-19)".

[0197]

[Chemical Formula 63]



[0198]

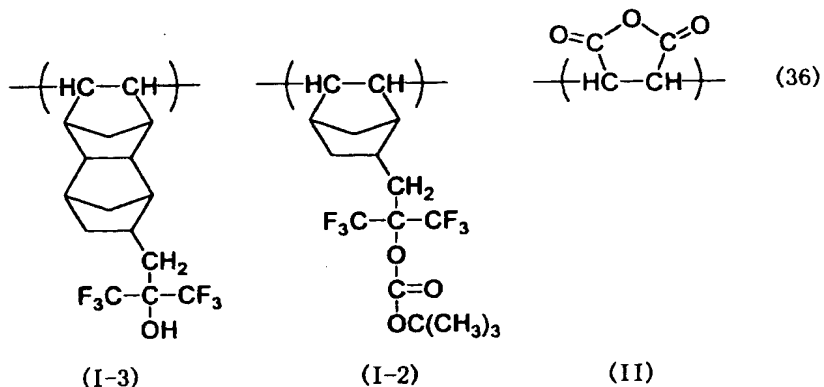
#### Synthesis Example 19

The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 6.83 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl) tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 13.25 g of 5-[2,2-bis(trifluoromethyl)-2-*t*-butoxycarbonyloxyethyl] bicyclo[2.2.1]hept-2-ene, and 4.92 g of maleic anhydride as monomers, to obtain 17 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-3), recurring unit (I-2), and recurring unit (II), shown in the following formulas (36), of 20:30:50, and having Mw of 4,200. This resin is referred to as a "resin (A-20)".

[0199]

[Chemical Formula 64]



[0200]

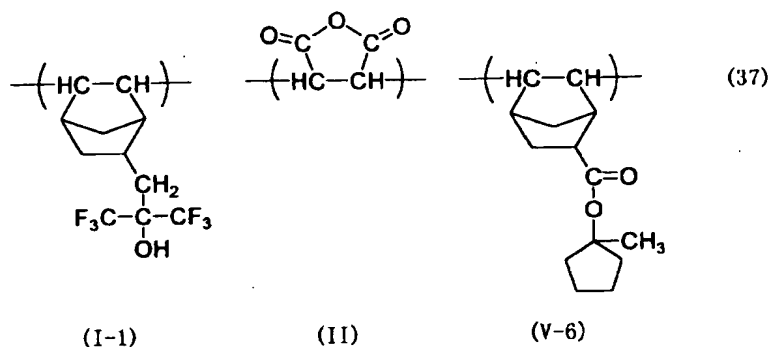
#### Synthesis Example 20

The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 8.07 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene, 7.21 g of maleic anhydride, and 9.72 g of 5-(1-methylcyclopentyloxycarbonyl)bicyclo[2.2.1]hept-2-ene as monomers, to obtain 20 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1), recurring unit (II), and recurring unit (V-6), shown in the following formulas (37), of 20:50:30, and having Mw of 4,800. This resin is referred to as a "resin (A-21)".

[0201]

[Chemical Formula 65]



[0202]

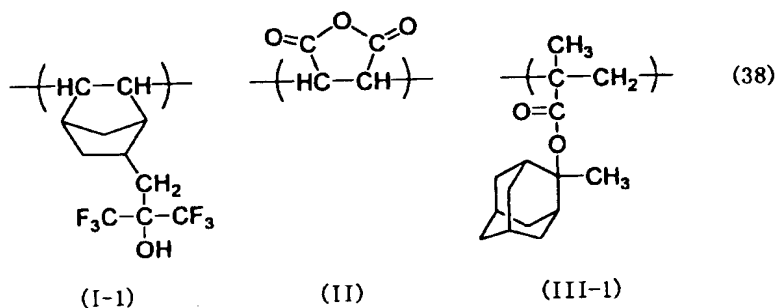
#### Synthesis Example 21

The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 7.67 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene, 6.86 g of maleic anhydride, and 10.47 g of 2-(2-methyl)adamantyl methacrylate as monomers, to obtain 16 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1), recurring unit (II), and recurring unit (III-1), shown in the following formulas (38), of 20:50:30, and having Mw of 5,800. This resin is referred to as a "resin (A-22)".

[0203]

[Chemical Formula 66]



[0204]

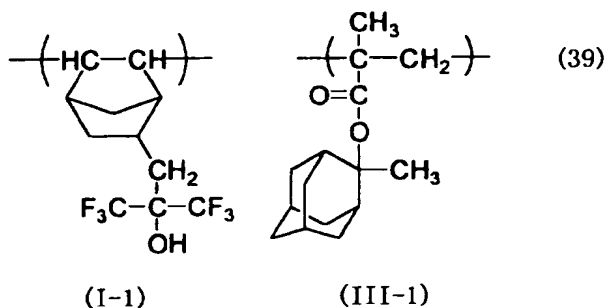
#### Synthesis Example 22

The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 32.69 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl) tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene and 17.31 g of 2-(2-methyl)adamantyl methacrylate as monomers, to obtain 18 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1) and recurring unit (III-1), shown in the following formulas (39), of 50:50, and having Mw of 5,900. This resin is referred to as a "resin (A-23)".

[0205]

[Chemical Formula 67]



[0206]

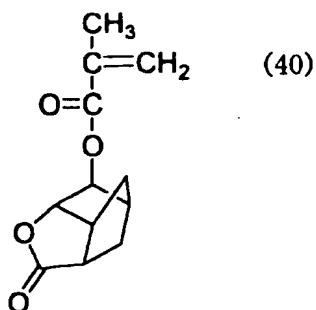
#### Synthesis Example 23

The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 24.50 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl) tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene, 17.31 g of 2-(2-methyl)adamantyl methacrylate, and 8.29 g of the compound shown by the following formula (40) as monomers, to obtain 20 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1), recurring unit (III-1), and recurring unit (III-3), shown in the following formulas (41), of 30:40:20, and having Mw of 5,700. This resin is referred to as a "resin (A-24)".

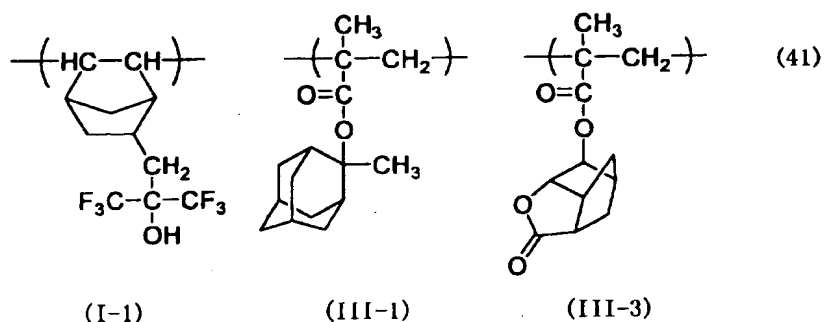
[0207]

[Chemical Formula 68]



[0208]

[Chemical Formula 69]



[0209]

#### Synthesis Example 24

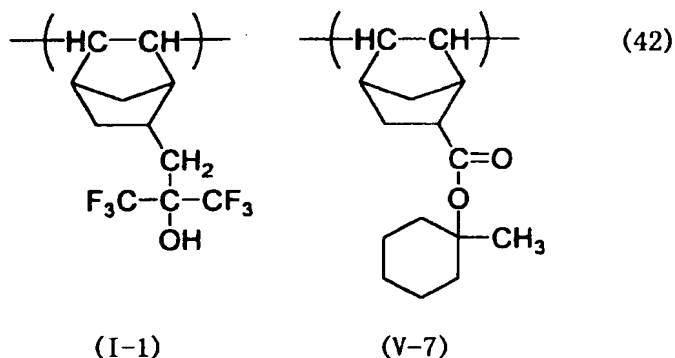
The same polymerization reaction as in the Synthesis Example 6 was carried out, except for using 5.53 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene and 4.47 g of 5-(1-methyl-1-cyclohexyloxycarbonyl)bicyclo[2.2.1]hept-2-ene as monomers, to obtain 7 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1) and recurring unit (V-7), shown in the following formulas (42), of

53:37, and having Mw of 30,700 and Mn of 14,500. This resin is referred to as a "resin (A-25)".

[0210]

[Chemical Formula 70]



[0211]

[Examples]

Examples 1-19 and Comparative Example 1

Each composition solution having components shown in Table 1 was evaluated. The evaluation results are shown in Table 3.

Components other than the resins (A-1) to (A-9), (A-12), (A-15), (A-18) to (A-25) shown in Table 1 are as follows.

#### Other resins

a-1: t-Butyl methacrylate/methyl  
methacrylate/methacrylic acid copolymer  
(copolymerization molar ratio = 40/40/20, Mw =  
20,000)

Acid generator (B)

B-1: Triphenylsulfonium nonafluoro-n-butanesulfonate

- B-2: Bis(4-t-butylphenyl)iodonium nonafluoro-n-butanesulfonate
- B-3: 1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiopheniumnonafluoro-n-butanesulfonate
- B-4: Bis(4-t-butylphenyl)iodonium perfluoro-n-octanesulfonate
- B-5: Nonafluoro-n-butanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-dicarbodiimide
- B-6: 4-n-Butoxy-1-naphthyltetrahydrothiophenium perfluoro-n-octanesulfonate

[0212]

(C) Acid diffusion controller

- C-1: Tri-n-octylamine
- C-2: 3-Pyperidino-1,2-propanediol
- C-3: N-t-butoxycarbonyldicyclohexylamine
- C-4: N-t-butoxycarbonyl-2-phenylbenzimidazole
- C-5: Tetra-n-butylammoniumhydroxide

Other additives

- D-1: t-Butyl deoxycholate
- D-2: Di-t-butyl 1,3-adamantanedicarboxylate
- D-3: t-Butoxycarbonylmethyl deoxycholate
- D-4: 2,5-Dimethyl-2,5-di(adamantylcarbonyloxy)hexane

Solvent

- E-1: 2-Heptanone
- E-2: Cyclohexanone
- E-3: Propylene glycol monomethyl ether acetate

[0213]



[Table 1]

Table 1

Unit in parentheses (part by weight)

	Resin	Photoacid generator (B)	Acid diffusion controller	Other additives	Solvents
Example 1	A-1 (90)	B-1 (2.0)	C-2 (0.05)	D-1 (10)	E-1 (430) E-2 (100)
Example 2	A-2 (90)	B-2 (2.0)	C-3 (0.10)	D-2 (10)	E-1 (430) E-2 (100)
Example 3	A-3 (90)	B-4 (3.0)	C-4 (0.10)	D-2 (10)	E-1 (430) E-2 (100)
Example 4	A-4 (90)	B-3 (3.5)	C-4 (0.10)	D-3 (10)	E-1 (430) E-2 (100)
Example 5	A-5 (90)	B-2 (3.0)	C-2 (0.05)	D-3 (10)	E-1 (430) E-2 (100)
Example 6	A-6 (90)	B-4 (3.0)	C-3 (0.10)	D-2 (10)	E-1 (430) E-2 (100)
Example 7	A-7 (90)	B-4 (3.0) B-5 (2.0)	C-3 (0.10)	D-3 (10)	E-1 (430) E-2 (100)
Example 8	A-8 (90)	B-2 (3.0) B-5 (2.0)	C-4 (0.10)	D-3 (10)	E-1 (430) E-2 (100)
Example 9	A-9 (90)	B-1 (2.0)	C-2 (0.05)	D-2 (10)	E-1 (430) E-2 (100)
Example 10	A-12 (90)	B-2 (3.0)	C-4 (0.10)	D-1 (10)	E-1 (430) E-2 (100)

[0214]

[Table 2]

Table 1 (Continued)

Unit in parentheses (part by weight)

	Resin	Photoacid generator (B)	Acid diffusion controller	Other additives	Solvents
Example 11	A-15 (90)	B-4 (3.0) B-5 (2.0)	C-4 (0.10)	D-3 (10)	E-1 (430) E-2 (100)
Example 12	A-18 (90)	B-4 (3.0)	C-3 (0.05) C-4 (0.05)	D-2 (10)	E-1 (430) E-2 (100)
Example 13	A-19 (90)	B-4 (2.5) B-5 (2.5)	C-3 (0.20)	D-3 (10)	E-3 (430) E-2 (100)
Example 14	A-20 (90)	B-2 (3.0) B-5 (2.0)	C-3 (0.15)	D-3 (10)	E-3 (530)
Example 15	A-21 (90)	B-6 (3.0)	C-2 (0.20)	D-2 (10)	E-1 (430) E-2 (100)
Example 16	A-22 (90)	B-4 (2.5) B-5 (2.5)	C-2 (0.17)	D-2 (10)	E-3 (530)
Example 17	A-23 (90)	B-6 (2.5)	C-3 (0.30)	D-3 (10)	E-3 (530)
Example 18	A-24 (90)	B-3 (3.5)	C-1 (0.15)	D-2 (10)	E-1 (430) E-2 (100)
Example 19	A-25 (88)	B-4 (2.0) B-5 (1.5)	C-5 (0.26)	D-4 (12)	E-3 (530)
Comparative Example 1	a-1 (90)	B-1 (2.0)	C-1 (0.05)	D-1 (10)	E-1 (530)

[0215]

[Table 3]

Table 2

	Thickness of resist film ( $\mu\text{m}$ )	Substrate	PB		PEB	
			Temp. ( $^{\circ}\text{C}$ )	Time (sec)	Temp. ( $^{\circ}\text{C}$ )	Time (sec)
Example 1	0.4	ARC	130	90	140	90
Example 2	0.4	ARC	130	90	140	90
Example 3	0.4	ARC	130	90	140	90
Example 4	0.4	ARC	130	90	140	90
Example 5	0.4	ARC	130	90	140	90
Example 6	0.4	ARC	130	90	140	90
Example 7	0.4	ARC	130	90	140	90
Example 8	0.4	ARC	130	90	140	90
Example 9	0.4	ARC	130	90	140	90
Example 10	0.4	ARC	130	90	140	90
Example 11	0.4	ARC	130	90	140	90
Example 12	0.4	ARC	130	90	140	90
Example 13	0.4	ARC	130	90	140	90
Example 14	0.4	ARC	130	90	140	90
Example 15	0.4	ARC	130	90	140	90
Example 16	0.4	ARC	130	90	140	90
Example 17	0.4	ARC	130	90	140	90
Example 18	0.4	ARC	130	90	140	90
Example 19	0.4	AR-19	130	90	150	90
Comparative Example 1	0.4	ARC	130	90	140	90

[0216]

[Table 4]

Table 3

	Radiation Transmittance (193 nm, %)	Sensitivity (J/m <sup>2</sup> )	Resolution ( $\mu$ m)	Developing Defect	Pattern Configuration
Example 1	75	73	0.15	0	Good
Example 2	72	74	0.15	0	Good
Example 3	69	69	0.15	0	Good
Example 4	71	70	0.15	0	Good
Example 5	68	74	0.15	0	Good
Example 6	73	72	0.15	0	Good
Example 7	70	68	0.15	0	Good
Example 8	75	77	0.15	0	Good
Example 9	70	69	0.15	0	Good
Example 10	68	71	0.15	0	Good
Example 11	70	74	0.15	0	Good
Example 12	71	71	0.15	0	Good
Example 13	74	72	0.15	0	Good
Example 14	71	74	0.15	0	Good
Example 15	74	77	0.15	0	Good
Example 16	72	69	0.15	0	Good
Example 17	67	76	0.15	0	Good
Example 18	68	72	0.15	0	Good
Example 19	73	79	0.13	0	Good
Comparative Example 1	62	150	0.18	45	Good

[0217]

[Effect of the Invention]

The radiation-sensitive resin composition of the present invention has high transmittance of radiation, exhibits high sensitivity, resolution, and pattern configuration as a chemically amplified resist, and is capable of producing semiconductors at a high yield while producing only a small

amount of resolution defects during microfabrication. The resin composition is expected to be an ideal material in the semiconductor field in which microfabrication technology will further advance in the future.

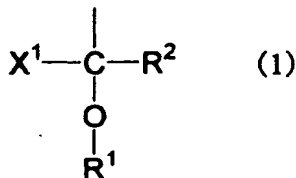
[Document Name] Abstract

[Abstract]

[Subject] To provide a novel radiation-sensitive resin composition, which has high transmittance of radiation, exhibits superior basic properties as a resist such as high sensitivity, resolution, and pattern configuration, and is capable of producing semiconductors at a high yield without producing developing defects during microfabrication.

[Means for the Solution] A radiation-sensitive resin composition comprising (A) an acid-dissociating group-containing resin having a structure represented by the following formula (1) and (B) a photoacid generator:

[Chemical Formula 1]



wherein  $\text{R}^1$  represents a hydrogen atom, a monovalent acid-dissociable group, an alkyl group which does not have an acid-dissociable group, or an alkylcarbonyl group which does not have an acid-dissociable group,  $\text{X}^1$  represents a linear or branched fluoroalkyl group having 1-4 carbon atoms, and  $\text{R}^2$  represents a hydrogen atom, a linear or branched alkyl group, or a linear or branched fluoroalkyl group.

[Selective Drawing] None

108824/2001

HISTORICAL INFORMATION ON APPLICANT

Identification No.

[000004178]

1. Date of Alteration

December 10, 1997

[Reason for Alteration]

Alteration of Name

Address:

2-11-24, Tsukiji, Chuo-ku, Tokyo

Name:

JSR Corporation

Certificate No. 2001-3053125

108824/2001

HISTORICAL INFORMATION ON APPLICANT

Identification No. [390009531]

1. Date of Alteration May 16, 2000

[Reason for Alteration] Alteration of Name

Address: Armonk, New York 10504, U.S.A.

Name: INTERNATIONAL BUSINESS MACHINES  
CORPORATION

Certificate No. 2001-3053125